

THE REACTION OF *t*-BUTYL ALCOHOL VAPOR WITH Hg 6(³P₁) ATOMS¹

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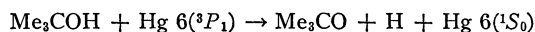
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ABSTRACT

The nature of the decomposition of *t*-butyl alcohol vapor, photosensitized by Hg 6(³P₁) atoms in a static system at room temperature, has been examined under a variety of conditions of continuous and intermittent illumination. The inhibiting effect of nitric oxide has also been studied, as well as the influence of added inert gas.

In the decomposition of pure substrate, the reaction products, with the initial quantum yields, Φ^0 , under continuous illumination in parenthesis, were: H₂ (0.045), Me₂CO (0.090), CO (0), CH₄ (0.015), C₂H₆ (0.030) together with lesser amounts of C₃H₈, Me₂CH, Me₃CMe, and Me₃COMe. On addition of nitric oxide, Me₃CONO, Me₂CO, N₂O, N₂, H₂O, and trace quantities of H₂ and CO were the only products observed.

The reaction

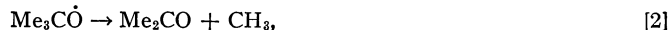


is proposed as the primary process in the decomposition and kinetic evidence is presented that the initially formed *t*-butoxy radicals possess excess energy and that their principal subsequent reaction is unimolecular cleavage into acetone and methyl. The results furthermore indicate that the substrate itself is quite inert to abstractive attack by the primary radicals.

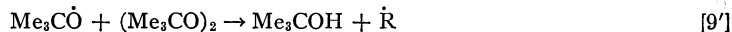
INTRODUCTION

Recent investigations of the vapor-phase reactions between Hg 6(³P₁) atoms and methanol (1, 2, 3), ethanol (4), and isopropanol (5, 6) have shown that scission of the O—H bond in each case is the dominant primary step in the reaction. What is more, the rate of abstraction of H-atoms from the substrate, by both primary fragments, rises with decreasing strength of the $\alpha(\text{C—H})$ bond, the site of abstractive attack. Thus, $\Phi(\text{H}_2)$ increases in the series MeOH, EtOH, *i*-PrOH, with values of 0.45 (2), 0.53 (4), and 0.72 (5) respectively. In the systems inhibited by nitric oxide, a similar trend is shown in the nitrite yield $\Phi(\text{RONO})$, in that as the rate of abstraction by RO increases with decreasing $D(\text{C—H})_\alpha$ in the substrate, there is a concomitant drop in $\Phi(\text{RONO})$. The foregoing predicts a marked change in the complexion of the reaction when no $\alpha(\text{C—H})$ bonds are present in the alcohol, suggesting the present study of *t*-butyl alcohol.

The photochemical decomposition of *t*-butyl alcohol has not been investigated previously. However, the photolysis of di-*t*-butyl peroxide has been the subject of several studies (7, 8, 9). It has been unequivocally demonstrated that the *t*-butoxy radical decomposes via



for which activation energies of 11.2 ± 2 kcal/mole (9) and 13.2 ± 2.4 kcal/mole (10) have been reported. McMillan and Wijnen re-investigated the photolysis (11), taking into account the reaction



and obtained an activation energy difference of 3 kcal/mole for $E_2 - E_9$.

Recently, however, McMillan (12) has found evidence for the formation of excited *t*-butoxy radicals in the photolytic system, thereby rendering uncertain the activation

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energy calculations previously reported. This author has also reported (13) the presence of vibrationally excited $\text{Me}_3\text{C}\dot{\text{O}}$ radicals in the photolysis of *t*-butyl nitrite, and has shown that such species can be collisionally deactivated by the addition of inert gas. Finally, in a recent study of the Hg-photosensitized decomposition of isopropanol (6) carried out in this laboratory, evidence was obtained for excited isopropoxy radicals in the reaction. Thus the formation of vibrationally excited alkoxy radicals appears to be a common characteristic of $\text{RO}\dot{\text{O}}$ -generating systems where the excitation energy exceeds the minimum required for primary bond-scission. For *t*-butyl alcohol, the exothermicity of the primary interaction with Hg $6(^3P_1)$ atoms is very close to the activation energy for the decomposition of the *t*-butoxy radical (*vide infra*) and the presence of excited species might be expected to have a profound effect on the system.

In the present investigation, the decomposition of *t*-butyl alcohol, photosensitized by Hg $6(^3P_1)$ atoms, has been studied to determine the mechanism and the role of energy-rich species in determining the course of the reaction.

EXPERIMENTAL

The essential details of apparatus, procedures, and purification techniques have been given in earlier papers in this series (2, 3, 6).

t-Butyl alcohol (British Drug Houses) was fractionally distilled, and a small, constant-boiling fraction was retained, prior to trap-to-trap distillation and degassing *in vacuo*. Analysis by gas liquid chromatography of the refined material proved the absence of impurities.

At the end of each experiment with pure substrate, products non-condensable at liquid nitrogen temperature were measured in a gas burette and analyzed by gas liquid chromatography, on a molecular sieves column, for CO and CH_4 , with hydrogen being determined by difference. The remaining fraction was treated in one of two ways: (a) removal of the fraction non-condensable at -98° (methanol slush) for hydrocarbon product analysis on a silica gel column, or, (b) analysis of the complete fraction via didecyl phthalate, $\beta\beta'$ -oxydipropionitrile, or Carbowax 20M columns, for acetone and methyl *t*-butyl ether. Duplicate runs were carried out at each exposure period (*t*) to allow both procedures to be used.

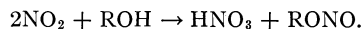
For the NO-inhibited reaction, products non-condensable at liquid nitrogen temperature, consisting largely of NO, were pumped off (except at $t = 30$ minutes where mass spectrometric analysis was performed). Subsequently, the fraction non-condensable at -130° (*n*-pentane slush) was removed and analyzed on the silica-gel column for N_2O . Finally, the remainder of the products was withdrawn and acetone and *t*-butyl nitrite yields determined with a didecyl phthalate or Carbowax 20M column.

In the intermittent illumination studies, the total yield of products non-condensable at -196° was determined, after which the sample was analyzed by mass spectrometry. In these runs the condensable products were not examined.

An attempt was made to determine the nature of any cell deposit formed in the reaction. In contrast to the alcohol systems previously studied (2, 4, 5), where the formation of a non-volatile product on the walls of the reaction cell could be readily discerned visually after approximately 2 to 4 hours of irradiation, none was apparent in the present system. Infrared spectra of chloroform washings of the cell were taken, but only after about 36 hours of reaction could a weak OH-bond absorption be detected. When the complicating effects of prolonged exposure are considered, however, these results must be regarded as inconclusive with respect to the formation of any glycol, although the results obtained in general indicate that the production of a small amount of glycol is likely.

Light intensities were determined with propane as actinometer (14), using the differential method of Back (15) to obtain a constant value for $d[\text{H}_2]/dt$. The values obtained, in $\mu\text{einstains/minute}$ were: 1.08 (intermittent illumination) and 2.62 and 2.53 (steady illumination).

In experiments where both NO and CF_4 were added, special precautions were necessary to avoid the complicating effects of the dark reaction previously found in the isopropanol system under the same conditions (6). Blank runs showed that unless NO and CF_4 are stored together for at least 12 hours and subsequently distilled into the reaction cell containing the alcohol, at a temperature at which NO_2 has negligible vapor pressure, i.e. -130° , the NO_2 formed by reaction of NO with trace quantities of oxygen present in the CF_4 , reacts with the alcohol to form *t*-butyl nitrite in appreciable quantities. Fairlie *et al.* (16) have studied the kinetics of this reaction in the liquid phase and these authors suggest that the overall reaction can be represented by



In the present study, as in the isopropanol work (6), it was found that the reaction could be eliminated by ensuring the absence of NO_2 in any gas admixed with pure *t*-butyl alcohol vapor.

RESULTS

As reaction products for the decomposition of *t*-butyl alcohol, at a pressure of 35 mm and at room temperature, H_2 , CO , CH_4 , Me_2CO , C_2H_6 , C_3H_8 , Me_3CH , Me_4C , and Me_3COMe were observed. A detectable yield of water was not observed. A specific search was made for isobutylene oxide and di-*t*-butyl peroxide but these products apparently do not form in this system. When the reaction was run in the presence of nitric oxide, the products, Me_3CONO , N_2O , H_2O , N_2 , Me_2CO , as well as trace quantities of CO and H_2 were found, and at the same time the yields of hydrocarbon products and methyl *t*-butyl ether were completely suppressed. No search was made for products of the methyl radical-nitric oxide reaction.

The uninhibited reaction was first examined under continuous illumination and the results, as a function of duration of exposure, are summarized as follows: Fig. 1, $\Phi(H_2)$, $\Phi(CO)$, $\Phi(CH_4)$; Fig. 2, $\Phi(Me_2CO)$, $\Phi(C_2H_6)$; Fig. 3, $\Phi(Me_4C)$, $\Phi(Me_3CH)$, $\Phi(Me_3COMe)$, $\Phi(C_3H_8)$.

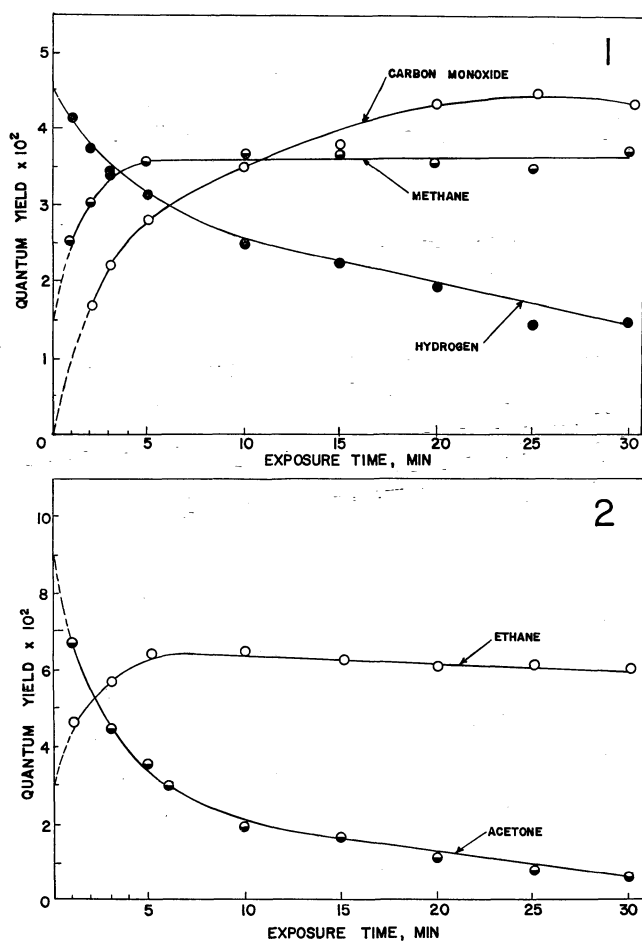


FIG. 1. Mean quantum yield of hydrogen, ●, carbon monoxide, ○, and methane, ◐, as a function of exposure time for 35 mm pure *t*-butyl alcohol.

FIG. 2. Mean quantum yield of acetone, ●, and ethane, ○, as a function of exposure time for 35 mm pure *t*-butyl alcohol.

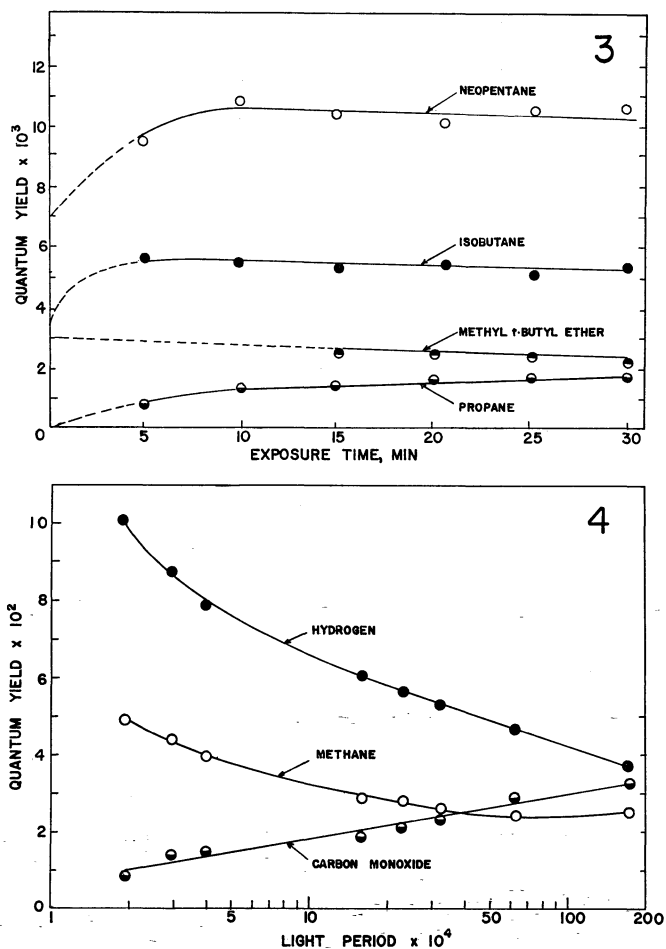


FIG. 3. Mean quantum yield of neopentane, \circ , isobutane, \bullet , methyl *t*-butyl ether, \ominus , and propane, \ominus , as a function of exposure time for 35 mm pure *t*-butyl alcohol.

FIG. 4. Quantum yield of hydrogen, \bullet , methane, \circ , and carbon monoxide, \ominus , as a function of light period, t_L , for a constant dark period of 160 msec for 35 mm pure *t*-butyl alcohol under intermittent illumination.

Under intermittent illumination, the effect of varying the light period, t_L , at a constant dark period, t_D , of 160 msec, on the yields of hydrogen, carbon monoxide, and methane was determined and the results are presented in Fig. 4.

The results obtained in the NO-inhibited reaction are given in Fig. 5. The reported quantum yields have been corrected for competitive quenching by nitric oxide, which was present at a pressure of 10 mm, assuming a quenching cross section, σ_Q , of 15 \AA^2 for *t*-butyl alcohol. The resulting correction factor was 1.7. For 30 minutes of exposure, the other products, water excepted, were determined by mass spectrometry and the values found were: $\Phi(\text{N}_2) = 2.7 \times 10^{-2}$, $\Phi(\text{CO}) = 8.8 \times 10^{-3}$, and $\Phi(\text{H}_2) = 7.6 \times 10^{-4}$.

The effect of adding the inert gas, CF_4 , on the uninhibited reaction is shown in Figs. 6 and 7. Figure 6 gives the results of a series of runs wherein the yield of acetone was determined as a function of $P(\text{CF}_4)$. Here, a short exposure time of 3.0 minutes was employed to minimize the complicating effects of secondary acetone decomposition. One additional

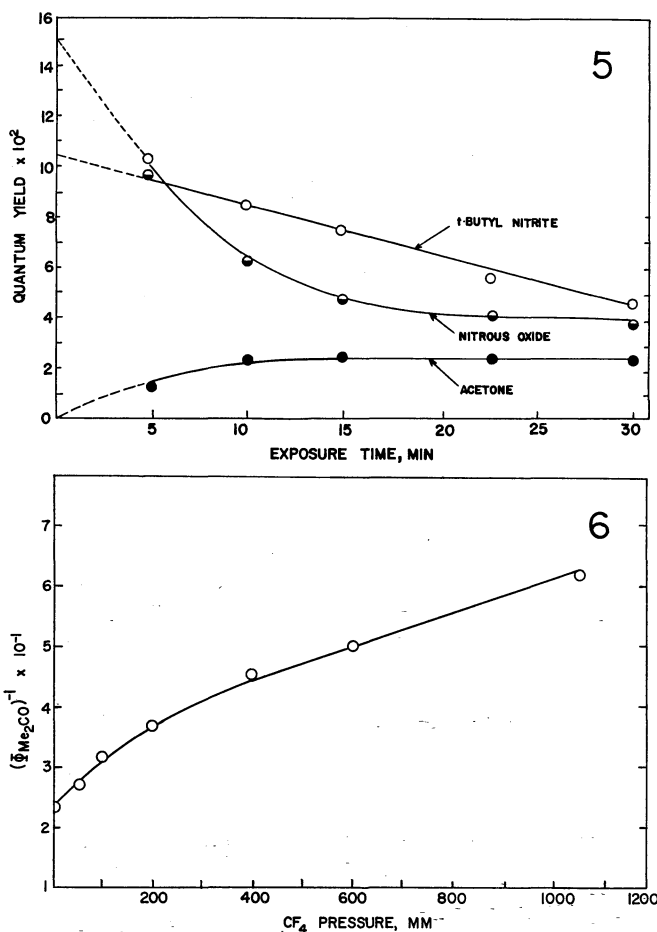


FIG. 5. Mean quantum yield, corrected for competitive quenching by NO, for *t*-butyl nitrite, O, nitrous oxide, ●, and acetone, ●, as a function of exposure time for 10 mm NO and 35 mm *t*-butyl alcohol.

FIG. 6. The reciprocal of the acetone quantum yield as a function of carbon tetrafluoride pressure for 35 mm *t*-butyl alcohol at an exposure time of 3 minutes.

run was performed with the *t*-butyl alcohol- CF_4 system, at an exposure time of 10 minutes, in which $\Phi(H_2)$ was determined by mass spectrometry to be 1.4×10^{-2} , for $P(CF_4) = 444$ mm. The addition of inert gas causes a marked decrease in the acetone yield, but the plot of $1/\Phi(Me_2CO)$ vs. $P(CF_4)$ does not give the expected straight line (Fig. 6). In a separate series of experiments, the influence of CF_4 pressure on the yields of isobutane and neopentane was determined. These results are given in Fig. 7. In this series an exposure time of 12 minutes was employed to allow product yields to attain levels consistent with accurate analysis. As shown in the figures, however, even under these conditions, the yields drop off to very small but finite values at $P(CF_4) > 150$ mm. The experimental error in the minute yields at high pressures is unfortunately too large to allow a meaningful plot of reciprocal quantum yields over the entire pressure range.

Finally, the yields of *t*-butyl nitrite and acetone, from the decomposition of a mixture of 35 mm *t*-butyl alcohol and 10 mm nitric oxide, were determined in a series of runs with exposure time = 5 minutes, as a function of CF_4 pressure up to $P(CF_4) = 900$ mm. The results are presented graphically in Fig. 8.

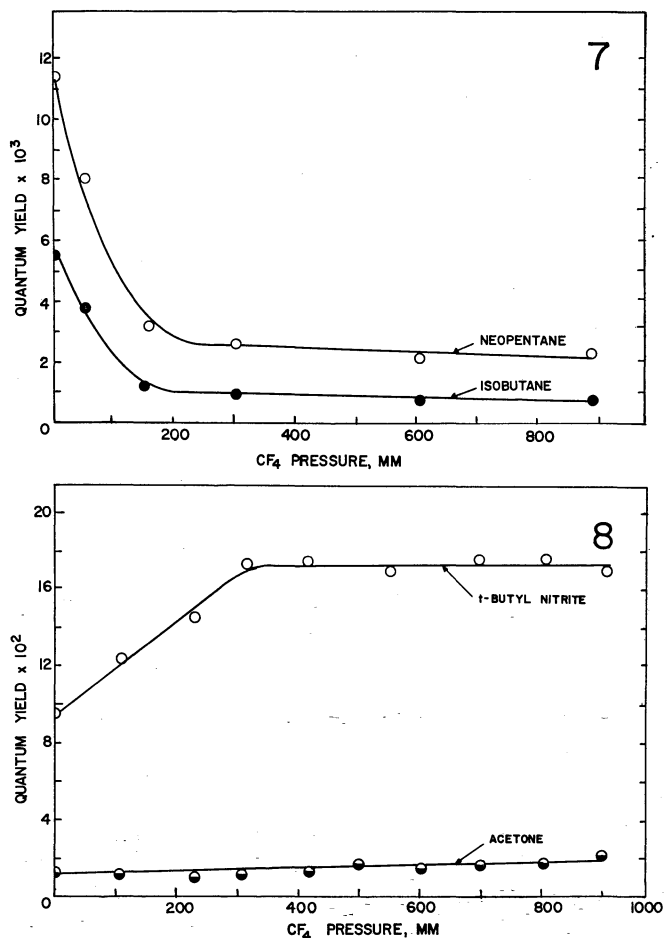


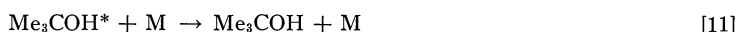
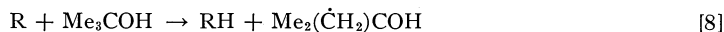
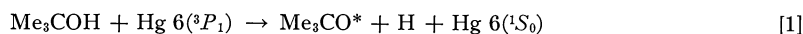
FIG. 7. The quantum yields of neopentane, \circ , and isobutane, \bullet , as a function of carbon tetrafluoride pressure, for 35 mm *t*-butyl alcohol at an exposure time of 12 minutes.

FIG. 8. The quantum yields of *t*-butyl nitrite, \circ , and acetone, \bullet , as a function of carbon tetrafluoride pressure, for 35 mm *t*-butyl alcohol and 10 mm nitric oxide at an exposure time of 5 minutes. The yields have been corrected for competitive quenching by nitric oxide.

DISCUSSION

The results obtained are consistent with the occurrence of O—H bond scission in the primary process. The appearance of *t*-butyl nitrite as the major heavy product in the NO-inhibited system, the formation of methyl *t*-butyl ether in the uninhibited decomposition, and the close correspondence of the products to those found in the photolysis of the peroxide, where the production of *t*-butoxy radicals has been unequivocally established, all indicate the formation of *t*-butoxy radicals in the decomposition of *t*-butyl alcohol. The fact that nitrous oxide, nitrogen, and water are formed when NO is added, is evidence for the presence of HNO (*vide infra*) and thus, for the formation of hydrogen atoms. The formation of an excited molecule in the primary step can be ruled out, since increasing inert gas pressure in the NO-inhibited reaction results in an increased nitrite yield, whereas an excited molecule would be collisionally deactivated and reduction of product yields would occur.

The following mechanism is proposed to account for the observed results.



where, $\text{R} = \text{Me}_3\text{CO}$, CH_3 , H , Me_3C , OH ; and $\text{R}'\text{H} = \text{Me}_2\text{CO}$, C_2H_6 .

Since acetone and methyl radicals are the known decomposition products of *t*-butoxy radicals, and since the presence of this radical has been confirmed, reaction [2] is proposed. The following stoichiometric considerations show [2] to be the sole source of CH_3 . In the initial stages of the reaction, methyl radicals evidently give rise to methane, ethane, methyl *t*-butyl ether, and neopentane, and thus their initial quantum yield is given by

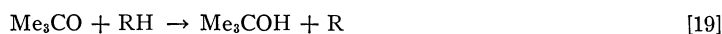
$$\Phi^{\circ}(\text{CH}_3) = \Phi^{\circ}(\text{CH}_4) + 2\Phi^{\circ}(\text{C}_2\text{H}_6) + \Phi^{\circ}(\text{Me}_3\text{COCH}_3) + \Phi^{\circ}(\text{Me}_3\text{CCH}_3). \quad [16]$$

Substitution of the appropriate values from Figs. 1, 2, and 3 gives a value of 8.5×10^{-2} for $\Phi^{\circ}(\text{CH}_3)$. On the basis of reaction [2] alone, $\Phi^{\circ}(\text{Me}_2\text{CO})$ should have the same value. Figure 2 shows that the value is 9.0×10^{-2} , which is in agreement with the value for $\Phi^{\circ}(\text{CH}_3)$ from equation [16], within experimental error.

Although the results showed that abstraction reactions involving the substrate were apparently minor, this does not preclude abstraction from products or the formation of $\text{Me}_2(\dot{\text{C}}\text{H}_2)\text{COH}$ radicals, which give rise to other products or reform the substrate in a step analogous to reaction [10]. It is thus important to establish the contribution of abstraction reactions.

Considering first abstraction by CH_3 radicals, McMillan (11) found in the photolysis of di-*t*-butyl peroxide that only ca. 3% of the methyl radicals formed resulted in methane. Since no H-atoms were present in that system, it is only this fraction which arose by abstraction from substrate or products. In the present system, however, if equation [16] is applied at $t = 30$ minutes, the data show that 21% of CH_3 radicals give rise to methane. Thus, if the abstraction reaction proceeds, as may be expected, at the same rate here as in the peroxide case, only approximately 14% of the observed methane yield arises via the abstraction of an H-atom by CH_3 radicals. On this basis and evidence presented below for a high H-atom concentration, reaction [5] is the proposed principal mode of methane formation.

For *t*-butoxy radicals, McMillan and Wijnen (11) found that ca. 5% of this species resulted in *t*-butyl alcohol when the peroxide was photolyzed. However, in view of recent evidence (12) for excited radicals which decompose before abstraction can occur, the estimate of the fraction abstracting may be low when applied to Me_3CO radicals of normal energies. Nevertheless, such radicals react very slowly with primary C—H bonds. In the pyrolysis of di-*t*-butyl peroxide, the relative rates of the reactions



have been determined for a large number of hydrogen donors. Relevant to the present argument, k_{19}/k_2 has a value of 0.47 l mole^{-1} for $\text{RH} = \text{isopropyl benzene}$ (17) but is only 0.06 l mole^{-1} for $\text{RH} = \textit{t}$ -butyl benzene (18). An important point here is the possible effects of the residual energy possessed by Me_3CO^* , on the $(k_8+k_9)/k_2$ ratio (analogous to the k_{19}/k_2 ratio in the peroxide case). The energy of the $\text{Hg } 6(^3P_1)$ atom is 112 kcal/mole, while $D(\text{O—H})$ for *t*-butyl alcohol is reported to be 104 (19) and 102 (20) kcal/mole. If $D(\text{O—H})$ is taken as 103 ± 1 kcal/mole, the maximum excess energy which could be taken by Me_3CO^* is 9 ± 1 kcal/mole. Activation energies of 11.2 ± 2 kcal/mole (9) and 13.2 ± 2.4 kcal/mole (10) have been reported for reaction [2]. Thus the energetic probability of unimolecular decomposition is marginal and no meaningful prediction of the decomposition/abstraction ratio can be made. The results, however, indicate that unimolecular decomposition predominates.

Abstraction by hydrogen atoms may also be important. The reduction of $\Phi(\text{H}_2)$ from a value of 1.5×10^{-2} at $t = 30$ minutes to 7.6×10^{-4} when 10 mm nitric oxide is added indicates that at least 95% of the molecular hydrogen produced arises from H-atoms. A material balance requires that one hydrogen atom be formed along with each acetone molecule and methyl radical, since the latter products are formed in equal quantities initially. $\Phi^0(\text{Me}_2\text{CO})$ is 9.0×10^{-2} and this must also be the minimum value for the initial yield of H-atoms. The value is minimal, since any abstraction by Me_3CO radicals results in less acetone being formed than H-atoms. Since the initial yield of molecular hydrogen is 4.5×10^{-2} it first appears that most, if not all, of the hydrogen atoms produced recombine. We have seen, however, that ca. 86% of the methane is arising from $\text{CH}_3\text{—H}$ combination in [5]. Similarly, reaction [13] accounts for 86% of the isobutane formed. On this basis, the total yield of hydrogen atoms is given by

$$\Phi_{\text{H-atoms}}^0 = 2(\Phi_{\text{H}_2}^0 - \alpha \Phi_{\text{H}_2}^0) + \alpha \Phi_{\text{H}_2}^0 + 0.86 \Phi_{\text{CH}_4}^0 + 0.86 \Phi_{\text{Me}_3\text{CH}}^0 \quad [20]$$

where α is the fraction of molecular hydrogen arising through abstraction by H-atoms. Substitution of the appropriate values from Figs. 1 and 3 yields

$$\Phi_{\text{H-atoms}}^0 = 0.107 + \alpha 0.045. \quad [21]$$

Considering the derivation of an analogous equation for Me_3CO radicals, if β is defined as the fraction of Me_3CO abstracting H-atoms, then $(1-\beta)$ will be the fraction yielding acetone. Thus,

$$(1-\beta) \Phi_{\text{Me}_3\text{CO}}^0 = \Phi_{\text{Me}_2\text{CO}}^0, \quad [22]$$

$$\Phi_{\text{Me}_3\text{CO}}^0 = \Phi_{\text{Me}_2\text{CO}}^0 / (1-\beta). \quad [23]$$

Since the initial yields of *t*-butoxy radicals and hydrogen atoms must be the same, [23]

and [21] may be equated, and after substitution of the value for $\Phi_{\text{Me}_3\text{CO}}$ from Fig. 2, the resulting equation is:

$$0.107 - \alpha 0.045 = 0.090 / (1 - \beta). \quad [24]$$

Now the values of α and β cannot be determined from this single equation, but maximum values can be established. A reasonable assumption is that the minimum fraction of Me_3CO radicals that are abstracting is that observed for the decomposition of the peroxide (see above), thus $\beta = 0.05$. This value corresponds to a maximum of 13% of all H-atoms abstracted. Similarly, it would be unlikely that the amount of H-atom abstraction would be less than that for CH_3 radicals, i.e. 3% (and thus $\alpha = 0.07$). Substitution of this value into equation [24] yields 14% for the extent of abstraction by Me_3CO . Thus limits can be set on the contribution of abstraction reaction by H and Me_3CO as follows: 3% < % H-atoms abstracting < 13%; 5% < % Me_3CO radicals abstracting < 14%. Thus an estimate of the initial quantum yield of *t*-butyl alcohol disappearance can be obtained. The initial quantum yield of H-atoms and *t*-butoxy radicals is 0.100 ± 0.005 (from limiting values calculated above) and if the quantum yield of decomposition giving isobutyl radicals, 0.010, is added, we have that:

$$\Phi_{\text{-ROH}}^0 = 0.110 \pm 0.005.$$

The accumulated evidence points to a very high radical concentration in the system. Thus the reaction resulting in substrate reformation, observed with the other alcohols (2, 4, 5), should also be operative. Since the concentration of H-atoms is considerably higher here, reaction [10] should play an even more important role. Considering first the results of the sector experiments, as illustrated in Fig. 4, the observed increase in $\Phi(\text{H}_2)$ and $\Phi(\text{CH}_4)$ as the light period is made progressively shorter, is evident for the importance of reaction [10] in lowering the observed yields under steady illumination. As the mean concentration of H-atoms and *t*-butoxy radicals is decreased, the probability of reaction [2] will rise, and hence the concentration of H and CH_3 , relative to that of Me_3CO , will be increased, leading to an increased rate for reactions [4] and [5]. The similarity of the $\Phi(\text{H})$ and $\Phi(\text{CH}_4)$ curves in Fig. 4 also suggest similar modes of formation of these products.

Further evidence for the importance of the back reaction derives from the fact that when 444 mm CF_4 is added to the system (cf. Results) the hydrogen quantum yield for $t = 10$ minutes drops from a value of 2.49×10^{-2} (for $P(\text{CF}_4) = 0$) to 1.36×10^{-2} . As will be seen later, the main effect of added CF_4 is to quench excited *t*-butoxy radicals before decomposition occurs and thus raise their steady-state concentration. Under such conditions the rate of reaction [10] should increase and $\Phi(\text{H}_2)$ would be diminished.

The formation of isobutane and neopentane is also related to the occurrence of step [10]. In the decomposition of methanol (2), CH_3 radicals apparently resulted from the decomposition of energy-rich MeOH , in the reaction analogous to [12]. In that case, where the amount of back reaction was less than in the present system (because of the high rate of abstraction from the substrate) the atomic cracking reaction amounted to ca. 5% of the total decomposition at 50 mm methanol pressure (2) and 18% at 8 mm (1). With 35 mm *t*-butyl alcohol, the *t*-butyl radicals produced in reaction [12] account for ca. 10% of the total decomposition. The results of the series of runs with added CF_4 , shown in Fig. 6, also indicate that isobutane and neopentane result from $(\text{Me})_3\dot{\text{C}}$ radicals formed in step [12] in that, as the partial pressure of CF_4 is increased, there is evidently increased collisional deactivation of Me_3COH^* , thereby reducing the rates of [12], [13], and [14]. The

residual yield of Me_3CH and Me_4C may be due to a small fraction of the primary process yielding OH and $\text{Me}_3\dot{\text{C}}$ radicals. However, this fraction cannot exceed ca. 3%.

Figure 2 shows that acetone is undergoing very rapid secondary decomposition in the early stages of the reaction. As in the case of isopropanol (5), acetone may be decomposing by Hg-photosensitization or by photolysis, or both. The overall reaction can be expressed as

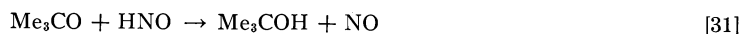
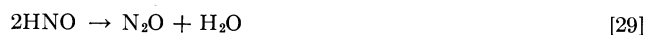


Using the mean quantum yield of acetone production for the first minute of exposure, $\Phi(\text{Me}_2\text{CO}) = 0.067$ (Fig. 2), there should be $0.067 \times 2.53 \times 30 = 5.09$ μmoles of this product after 30 minutes. Only 0.55 μmoles were actually found, indicating that 4.45 μmoles suffered secondary decomposition. Thus, in addition to the 5.09 μmoles CH_3 produced in reaction [2], there should be an additional yield of 2×4.54 μmoles from reaction [25], in all, a total of 14.2 μmoles of methyl radicals. Calculating from the observed yields, we found a value for the CH_3 yield at 30 minutes of 13.8 μmoles . The accountability in CO is not as satisfactory, in that, of the 4.54 μmoles predicted by the calculation, only 3.5 were found after 30 minutes of reaction. In view of the high H-atom concentration in the system, however, some of the missing CO may have disappeared in reactions with H-atoms, and this would likely be followed by dilution of the 1 μmole of HCO radicals among undetectable quantities of minor products.

Two factors may determine the decrease in $\Phi(\text{H}_2)$ with time, shown in Fig. 1. Secondary quenching by hydrogen itself, in addition to lowering the rate of reaction [1], will increase the concentration of hydrogen atoms, resulting in increasing importance of [10]. Secondary quenching by reaction products other than hydrogen will also diminish the rate of primary decomposition.

Methane and ethane, as shown in Figs. 1 and 2, increase in yield very rapidly with exposure time during the first ca. 5 minutes of reaction, and thereafter remain essentially constant. In the initial stages of the reaction, methyl radicals result solely from reaction [2], but as reaction [25] increases in importance, it will provide an additional source of methyl radicals. Thus the yields of CH_4 and C_2H_6 would be expected to rise rapidly as $\Phi(\text{Me}_2\text{CO})$ falls off (cf. Fig. 2), but level off when acetone had attained a steady-state concentration. Although the rate of the overall reaction [25] decreases very rapidly with time, this condition does not obtain until ca. 15–20 minutes. The fact that $R(\text{CH}_4)$ and $R(\text{C}_2\text{H}_6)$ reach constant values earlier may arise from their rate of formation in reaction [2] being diminished through a general decrease in the rate of step [1] with time, as the concentration of products capable of quenching a detectable fraction of the incident energy increases.

The following mechanism is proposed to account for the observed results in the presence of 10 mm nitric oxide: reactions [1] through [3] will be followed by the following reactions.



The reaction of H-atoms with nitric oxide has been discussed previously (6). There is probably, however, an additional step giving rise to N_2O , since the yield of H-atoms calculated from the stoichiometry of reactions [28] to [30] is inordinately high, and the water yield, though not determined quantitatively, was clearly smaller than that of N_2O .

Since the yields have been corrected for competitive NO quenching, using an assumed value of the quenching cross section for *t*-butyl alcohol, $\sigma_0^2 = 15 \text{ \AA}^2$, an attempt to obtain a quantitative correlation between yields in the inhibited and NO-free systems does not appear justified.

The marked decrease in $\Phi(\text{Me}_2\text{CO})$ with increasing CF_4 pressure shown in Fig. 7 indicates that excited *t*-butoxy radicals are the precursors of acetone. The observed results cannot be interpreted in terms of an excited molecule mechanism, since increased collisional deactivation would decrease the yield of Me_3CO radicals, and when NO is present (cf. Fig. 8 and discussion below), the nitrite yield would drop. Now if there is a simple competition between reactions [2], unimolecular decomposition, and [3] deactivation of Me_3CO^* , the plot of $1/\Phi(\text{Me}_2\text{CO})$ vs. $P(\text{CF}_4)$ should be linear, whereas the curve of Fig. 10 is not, particularly at low CF_4 pressures. This suggests (a) a second acetone-producing step only slightly affected by inert gas pressure, or (b) collisional deactivation of Me_3CO^* by a third body is not a simple function of the collision frequency. The latter is more attractive, since the results appear to exclude any acetone-producing reaction other than [2]. Hershenson and Benson (21) have recently suggested that the unimolecular decomposition of Me_3CO , produced in pyrolysis or photolysis, is pressure dependent. Thus the results here may be a combination of this effect and the "normal" removal of vibrational energy through collision.

The observed increase in nitrite yield as the pressure of CF_4 is increased, as shown in Fig. 8, can be ascribed to the dual effect of CF_4 in deactivating excited *t*-butoxy radicals and in removing excess energy from any nitrite formed by the combination of Me_3CO^* radicals and nitric oxide.

Since $\Phi(\text{Me}_2\text{CO})$ is essentially invariant with increasing inert gas pressure, the *t*-butoxy radicals giving rise to the "additional" nitrite formed under these conditions, must participate in a reaction other than unimolecular decomposition in the absence of inert gas, where the reaction mixture consists of 35 mm *t*-butyl alcohol and 10 mm nitric oxide. The two alternatives are abstraction and substrate reformation. However, the contribution of the latter reaction would not be expected to decrease with rising inert gas pressure since we have seen that with pure *t*-butyl alcohol $\Phi(\text{H}_2)$ decreases with increasing CF_4 pressure under these conditions, indicating an *increasing* role for the back reaction. Furthermore, it has been shown that a maximum of 14% Me_3CO^* radicals take part in the abstraction reaction in the absence of both nitric oxide and carbon tetrafluoride. Thus it is apparent that the addition of just 10 mm nitric oxide, greatly facilitates H-atom abstraction by *t*-butoxy radicals. The nitric oxide must cause a partial deactivation of Me_3CO^* to an energy level below the minimum required for reaction [2], but sufficiently high to overcome part of the activation energy requirement for abstraction from the substrate. A similar behavior was found by McMillan (13) in the photolysis of *t*-butyl nitrite - nitric oxide mixtures, where it was found that nitric oxide had an unexpectedly high efficiency in quenching excited alkoxy radicals. From these results, it is apparent that the quenching of excited *t*-butoxy radicals is not a simple collisional deactivation, and further investigation is evidently required to uncover the exact nature of this process.

In summary, the reaction of *t*-butyl alcohol vapor with $\text{Hg } 6(^3P_1)$ atoms produces excited *t*-butoxy radicals and hydrogen atoms in the primary interaction of substrate and

sensitizer. The principal mode of disappearance of *t*-butoxy radicals is unimolecular decomposition into acetone and methyl radicals. The alcohol is relatively inert to abstractive attack with the result that radical concentrations are high in the system and combination reactions are thus of considerable importance.

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