THE PHOTOLYSIS OF ACETONE IN THE PRESENCE OF TRIETHYLBORANE

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(Received November 13th, 1970; in revised form January 25th, 1971)

SUMMARY

The photolysis of acetone in the presence of triethylborane has been investigated at 20 and 126°. From an analysis of the hydrocarbons produced and the diminution of the rate of carbon monoxide formation, it is concluded that a reaction between the acetone triplets and triethylborane takes place and that this reaction produces ethyl radicals. The values of the rate constant of this reaction were found to be $\approx 1 \times 10^{11}$ and 3.4×10^{11} ml·mole^{-1}·s^{-1} at 20 and 126° respectively. The small temperature dependence of these values points to a very low activation energy. This result is similar to that previously found for the biacetyl/triethylborane system.

The rates of attack of methyl and ethyl radicals on triethylborane have also been measured.

INTRODUCTION

The vapor phase photolysis of acetone is now well understood[1]. At 3130 Å, most of the significant processes occur from the lower triplet, and their rate constants, as well as their pressure dependence, have been measured[1].

In a previous paper[2] we have reported that triethylborane is a reactive quencher of biacetyl triplets, and that this quenching involves the production of ethyl radicals. As it has been shown that the photolysis of acetone at low temperatures in the presence of triethylborane (TEB) also produces ethyl radicals[3], it was decided to investigate whether these radicals are produced by reaction of some excited species or of methyl and acetyl radicals with TEB.

Acetone was therefore photolysed with light of wavelength longer than 2900 Å in the presence of TEB at different temperatures, the volatile products being analyzed by gas chromatography. From our results it can be concluded that reactive quenching of acetone triplets by TEB is the main source of ethyl radicals in this system.

EXPERIMENTAL

Two Pyrex reaction cells were employed. One of them (100 ml) was thermostatted by means of a circulating water jacket. The other one (330 ml) was immersed

in a thermostatted oil bath. A nearly parallel light beam that illuminated the whole reaction cell was employed. Light from a medium pressure mercury lamp was filtered using two Pyrex glasses (2 mm thick). This cut off all radiation of wavelength shorter than 2900 Å.

The reactants were measured inside the reaction cell with a differential manometer. The second reactant was always admitted from a higher pressure to improve the mixing. As dead space was very low, this method assured reasonable mixing of the reactants. To measure the quantum yields, duplicate runs were done with pure acetone immediately before or after each run.

TEB was an Ethyl Corporation product. Acetone was an analytical grade reagent from Hopkins and Williams. The lack of any absorption in the 4000 Å region showed that the acetone contained less than 0.5×10^{-3} moles per cent of biacetyl. Both reagents were handled under high vacuum conditions and were purified by trap-to-trap distillation.

The reaction products were fractionated by low temperature traps into three fractions: (a) The fraction retained at $-100°$ was not analyzed. (b) The fraction retained at liquid nitrogen temperature was analyzed by gas chromatography on an alumina column. It consisted of ethane, ethylene, propane, n-butane and small amounts of propylene. (c) The fraction uncondensable at liquid nitrogen temperature was analyzed on molecular sieves. It consisted of methane and carbon monoxide.

RESULTS

Under the conditions employed in the present study, TEB does not react when irradiated by itself. Furthermore, dark runs of mixtures of TEB and acetone did not give any volatile product below 140°. No pressure change could be detected under the same conditions.

When acetone alone was photolyzed, the only products detected were carbon monoxide, methane and ethane. At 126° the carbon monoxide quantum yield was higher than $\phi(C_2H_6) + \frac{1}{2}\phi(CH_4)$ (see Table 2). On the other hand, at 107°, $\phi(CO)$ was lower than $\phi(C_2H_6) + \frac{1}{2}\phi(CH_4)$. At temperatures lower than 30°, only ethane and small amounts of methane were detected.

Results at low temperature

When the mixtures of TEB and acetone were photolyzed at 20°, the results shown in Table 1 were obtained.

In Fig. 1 a plot of the total amounts of methyl radicals produced relative to the amount of ethyl radicals is given as a function of the inverse TEB concentration. The rate of methyl radical formation was evaluated from eqn. (1) where the last term accounts for the ethane arising from the methyl radical recombination.

$$R(CH_3) = R(CH_4) + R(C_3H_8) + [R(C_3H_8)]^2/2\,R(C_4H_{10}) \tag{1}$$

The rate of ethyl radical formation was evaluated from eqn. (2) where the last term is a correction to account for the ethane produced by methyl radical recombination

$$R(C_2H_5) =$$
$$2\,R(C_4H_{10}) + R(C_2H_4) + R(C_3H_8) + R(C_2H_6) - [R(C_3H_8)]^2/4\,R(C_4H_{10}) \tag{2}$$

TABLE 1

EXPERIMENTAL RESULTS AT 20°C

Rates are given in 10^{-12} mole·ml^{-1}·s^{-1}. Concentrations are given in 10^{-6} mole/ml.

| Total concn.	[TEB]	$R(CH_4)$	$R(C_2H_6)$	$R(C_2H_4)$	$R(C_3H_8)$	$R(C_4H_{10})$
1.69	0.83	0.22	0.60	0.03	0.11	
2.44	0.84	0.22	0.70	0.09	0.22	
3.27	0.0	~0.08	0.10	0.0	0.0	0.0
3.34	0.85	0.19	1.27	0.26	0.31	
3.58	0.29	0.23	1.21	0.16	0.27	
4.12	0.86	0.12	2.33	0.20	0.33	
4.15	0.81	0.27	1.97	0.29	0.37	
4.15	0.85	0.25	1.57	0.32	0.37	
4.23	0.85	0.23		0.34	0.40	
4.55	1.23	0.24	2.12	0.28	0.35	
5.16	1.66	1.19	3.05	0.15	0.27	1.25
5.31	0.22	0.26	1.70	0.35	0.63	
5.31	0.22	0.21	1.96	0.31	0.63	
5.31	0.23	0.23	2.46	0.19	0.48	1.50
5.31	0.25	0.26	1.81	0.27	0.59	
5.31	0.27	0.24	1.33	0.24	0.52	1.97
5.31	0.28	0.24	1.96	0.21	0.52	1.93
5.31	0.42	0.21	1.99	0.30	0.57	
5.31	0.48	0.22	1.48	0.37	0.71	
5.31	0.58	0.14	2.01	0.34	0.45	
5.31	0.94	0.23	2.13	0.28	0.44	2.10
5.31	1.39	0.22	2.39	0.18	0.35	1.32
5.31	1.47	0.27	2.07	0.21	0.39	1.93
5.31	1.59	0.31	2.39	0.42	0.64	
5.31	1.59	0.21	2.74	0.31	0.60	
5.31	1.59	0.45	3.24	0.36	0.25	
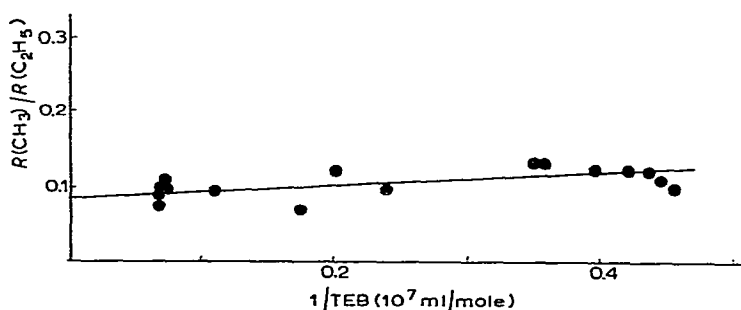
Fig. 1. $R(CH_3)/R(C_2H_5)$ as a function of the inverse TEB concentration. Temp. 20°. Total concentration 5.31×10^{-6} mole/ml.

In those runs in which butane was not measured its rate of formation was evaluated from the rate for ethylene.

Results at 107 and 126°

The experimental results obtained at 126° are given in Table 2, where some of the data obtained at 107° have also been included.

TABLE 2

EXPERIMENTAL RESULTS AT TEMPERATURES HIGHER THAN 100°

Rates are given in 10^{-12} mole·ml^{-1}·s^{-1}. Concentrations are given in 10^{-6} mole/ml.

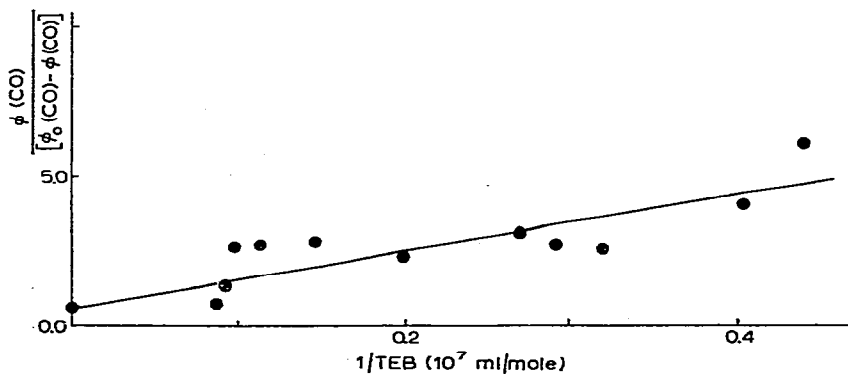| Total concn.	[TEB]	R(CO)	R(CH$_4$)	R(C$_2$H$_6$)	R(C$_2$H$_4$)	R(C$_3$H$_8$)	R(C$_4$H$_{10}$)
	107°						
2.5	0.0	6.68	1.16	8.5	0.0	0.0	0.0
2.5	0.0	7.10	1.01	9.0	0.0	0.0	0.0
2.8	0.27	5.8	4.0	3.3		1.18	0.34
3.2	0.64	4.8	3.8	4.6	0.16	0.53	0.15
3.72	1.22	3.6	4.2	3.1	0.08	0.44	0.21
3.88	1.33	3.9	4.1	4.0	0.12	0.26	0.21
	126°						
3.02	0.0	4.50	1.77	2.83	0.0	0.0	0.0
3.02	0.0	4.50	2.41		0.0	0.0	0.0
3.02	0.0	4.47	2.94	2.36	0.0	0.0	0.0
3.02	0.23	3.57	4.44	1.30	0.07	0.41	0.25
3.02	0.25	3.32	4.05	1.12	0.08	0.49	0.08
3.02	0.31	2.83	4.06	3.43	0.05	0.33	
3.02	0.34	2.91	4.02	1.43	0.11	0.30	0.11
3.02	0.37	2.99	5.33	7.84	0.09	0.33	0.21
3.02	0.50	2.71	3.43				
3.02	0.67	2.59	4.11	1.59	0.13	0.13	0.08
3.02	0.86	2.36	3.26	2.74	0.12	0.12	0.15
3.02	1.02	2.19	3.03	4.33	0.12	0.09	0.04
3.02	1.08	1.64	3.00				
3.02	1.13	1.24	2.42				
3.90	0.0	6.11	2.71				
3.90	1.17	2.83	4.99				

Fig. 2. $\phi(CO)/[\phi_0(CO)-\phi(CO)]$ as a function of inverse TEB concentration. Temp. 126°. Total concentration 3.02×10^{-6} mole/ml.

In Fig. 2 a plot of $\phi(CO)$ divided by $\phi_0(CO)-\phi(CO)$ [where $\phi_0(CO)$ is the carbon monoxide quantum yield in the photolysis of pure acetone] is given as a function of the inverse TEB concentration.

When 1,3-butadiene was added to the acetone instead of TEB, the diminution of carbon monoxide was nearly independent of the concentration of 1,3-butadiene (1,3-butadiene pressures from 5 to 10 mm). Under these conditions

$$\phi(CO)/\phi_0(CO) - \phi(CO) = 0.6$$

DISCUSSION

The mechanism of the photolysis of acetone at long wavelength in the presence of a reactive quencher can be represented by the set of reactions (3)–(9) where it has

$$A + h\nu \rightarrow {}^3A^* \tag{3}$$

$${}^3A^* \rightarrow CH_3^\cdot + CH_3CO^\cdot \tag{4}$$

$${}^3A^* + M \rightarrow {}^3A + M \tag{5}$$

$${}^3A + (M) \rightarrow CH_3^\cdot + CH_3CO^\cdot + (M) \tag{6}$$

$${}^3A^\cdot \rightarrow A + h\nu \tag{7}$$

$${}^3A \rightarrow A^* \tag{8}$$

$${}^3A + Q \rightarrow \text{Products} \tag{9}$$

been assumed that almost all the excited molecules cross over to the triplet state. It must be pointed out that if the decomposition arose from the excited singlet this would not modify the following discussion.

If TEB is the added quencher and the reactive quenching involves the production of an ethyl radical, the following reactions will occur:

$${}^3A + TEB \rightarrow C_2H_5^\cdot + P^\cdot \tag{10}$$

$$C_2H_5^\cdot + C_2H_5^\cdot \rightarrow C_4H_{10} \tag{11}$$

$$C_2H_5^\cdot + C_2H_5^\cdot \rightarrow C_2H_6 + C_2H_4 \tag{12}$$

$$CH_3^\cdot + CH_3^\cdot \rightarrow C_2H_6 \tag{13}$$

$$C_2H_5^\cdot + CH_3^\cdot \rightarrow C_3H_8 \tag{14}$$

$$C_2H_5^\cdot + CH_3^\cdot \rightarrow CH_4 + C_2H_4 \tag{15}$$

$$C_2H_5^\cdot + TEB \rightarrow C_2H_6 + R^\cdot \tag{16}$$

$$CH_3^\cdot + TEB \rightarrow CH_4 + R^\cdot \tag{17}$$

$$C_2H_5^\cdot + A \rightarrow C_2H_6 + A^\cdot \tag{18}$$

$$CH_3^\cdot + A \rightarrow CH_4 + A^\cdot \tag{19}$$

The formation of propene has been discussed elsewhere[4] and is due to a secondary reaction of R$^\cdot$.

Low-temperature results

The presence of ethyl radicals in the system can be inferred from the hydrocarbons produced and by their relative rates of production as $R(C_2H_4)/R(C_4H_{10})$ is nearly 0.13, in agreement with the expected value from the disproportionation/combination ratio of ethyl radicals[5].

That the ethyl radicals are mainly produced by reaction (10) and not by reaction (20) or by the acetyl radicals (either in a bimolecular reaction or thorugh the

$$CH_3^* + TEB \rightarrow C_2H_5^* + CH_3BEt_2 \qquad (20)$$

formation of biacetyl and its subsequent reaction with TEB[2]) can be deduced from the following facts:

(a). The $\phi(C_2H_5)$ obtained at 20° with 15 mm of added TEB is nearly one. On the other hand, the decomposition quantum yield under similar conditions can be estimated from the data of O'Neal[6] as being smaller than 0.20 if the same efficiency as M is assumed for TEB and acetone.

(b). The rate of reaction (20) has been measured in the azomethane/TEB system[4] and found to be smaller than the rate of reaction (17). As in the present system eqn. (21) holds, we have then that the rate of reaction (20) must be smaller than the

$$R_{15} + R_{17} + R_{19} = R(CH_4) \qquad (21)$$

rate of methane production. The experimental results show that the relations (22) and (23) hold. This fact shows that reaction (20) cannot be the main source of ethyl radicals in the present system.

$$R(C_2H_5^*) > 20 \, R(CH_4) \qquad (22)$$

$$R(C_2H_5) > 20 \, R_{20} \qquad (23)$$

(c). The number of acetyl radicals produced can be estimated from the rate of methyl radical production. The proposed set of reactions leads to eqn. (24). If the ethyl

$$R(CH_3CO^*) = R(CH_3^*) + R_{20} \sim R(CH_3^*) + R(CH_4) \qquad (24)$$

radicals were produced by reactions of the acetyl radicals or of some of its reaction products, relation (25) would hold. On the other hand, eqn. (26) is found at TEB

$$R(C_2H_5^*)/R(CH_3CO^*) \leqslant 1 \qquad (25)$$

pressures higher than 5 mm.

$$R(C_2H_5^*)/R(CH_3CO^*) > 5 \qquad (26)$$

From the preceding discussion it can be concluded that reaction (10) can be considered as the main source of ethyl radicals. Furthermore, the high quantum yield of ethyl radicals shows that this reactive quenching is the main reaction of acetone triplets in the presence of TEB.

If reactions (11) to (19) are the main reactions of methyl and ethyl radicals, their rates of production can be evaluated from eqns. (1) and (2). Combination of other radicals present in the system (P*, R*, A* or CH_3CO^*) with methyl and ethyl radicals should make the use of eqns. (1) and (2) questionable. But, as the rates of recombination of these radicals with methyl and ethyl radicals should be quite similar, it can be shown that eqn. (27) will approximately hold, even when a significant

$$(R_4 + R_6)/R_{10} = (R(CH_3^*) + R_{20})/(R(C_2H_5^*) - R_{20}) \qquad (27)$$

fraction of the small radicals are being consumed by recombination with higher radicals. The correction by reaction (20) is a minor one and is easily accounted for as k_{20} has been measured[4].

From reactions (3) to (10) relation (28) can be concluded, where M measures

$$\frac{R_4+R_6}{R_{10}} = \frac{K_4}{k_5 \cdot M} + \frac{1}{k_{10}} \cdot \left[\frac{k_4}{k_5 \cdot M} \cdot (k_6+k_7+k_8) + k_6\right] \cdot \frac{1}{[TEB]} \tag{28}$$

the total concentration and k_6 will be pressure-dependent. To obtain eqn. (28) the same third body efficiency has been assumed for TEB and acetone[2,7]. In eqn. (28), k_4 is the only rate constant that will depend upon the initial wavelength. Then, if both M and the wavelength are kept constant, $(R_4+R_6)/R_{10}$ should depend linearly on the inverse TEB concentration. This plot, with $(R_4+R_6)/R_{10}$ evaluated from eqns. (1), (2) and (27), is shown in Fig. 1. From this plot, the following values can be derived

$$k_4/k_5 = 4.5 \times 10^{-7} \text{ mole/ml}$$

and

$$k_{10} \approx 1 \times 10^{11} \text{ ml} \cdot \text{mole}^{-1} \cdot \text{s}^{-1}$$

if the values of k_6, k_7 and k_8 previously reported are employed[1]. The value found for k_4/k_5 is higher than that previously reported[1] for the 3130 Å radiation (1.5×10^{-7} mole/ml). As k_4 is extremely sensitive to the initial energy, this discrepancy may reflect a shorter average wavelength absorbed under the present conditions.

Further support for the proposed mechanism can be obtained from the effect of total concentration. From the small slope of Fig. 1 and the fact that $k_8 > k_6$ at 20°, it can be concluded that most of the methyl radicals produced when 15 mm of TEB are present, arise from reaction (4). If under these conditions the contribution of reaction (6) to methyl radical formation is neglected, eqn. (28) reduces to eqn. (29).

$$R_4/R_{10} = [k_4/(k_5 \cdot M)] \cdot [1 + k_8/(k_{10} \cdot [TEB])] \tag{29}$$

A plot of R_4/R_{10} against $1/M$ at 15 mm constant TEB pressure is shown in Fig. 3. From this plot a value of

$$k_4/k_5 = 4.5 \times 10^{-7} \text{ mole/ml}$$

can also be obtained, in good agreement with that obtained from Fig. 1.

High-temperature results

It is generally assumed[8] that, working at low intensities and at temperatures higher than 100°, acetyl radicals can be considered as reacting almost exclusively by
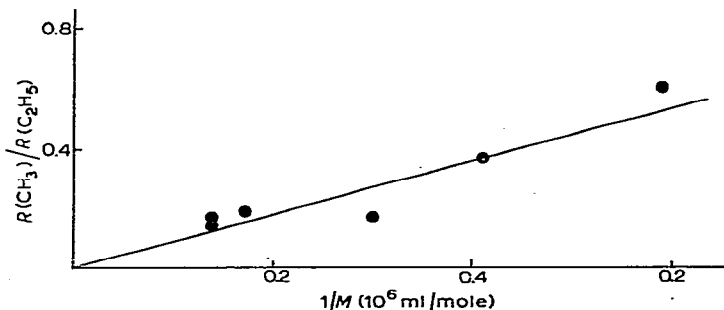

Fig. 3. Effect of total concentration in $R(CH_3)/R(C_2H_5)$ at constant TEB concentration. Temp. 20°. [TEB] 0.85×10^{-6} mole/ml.

reaction (30) provided that there is no reaction of these radicals other than decomposition, combination and disproportionation.

$$CH_3CO^\cdot \,(+M) \rightarrow CH_3^\cdot + CO\,(+M) \tag{30}$$

At 107° the mass balance of the runs of acetone alone $2\,[\phi(CO)/\phi(CH_3^\cdot)] < 1$ shows that reaction (30) is competing with other reactions of the acetyl radicals. On the other hand, the results obtained at 126° show that under these conditions it can be considered that the acetyl radicals are reacting nearly quantitatively by reaction (30). Under these conditions eqn. (31) can be then assumed.

$$R(CO) = R_4 + R_6 \tag{31}$$

If we assume that eqn. (31) also holds when TEB is added, then the proposed mechanism leads to eqn. (32), where $\phi(CO)$ is the quantum yield of carbon monoxide

$$\frac{\phi(CO)}{\phi_0(CO) - \phi(CO)} = \frac{k_4}{k_5 \cdot M} \cdot \frac{k_6 + k_7 + k_8}{k_6} + \frac{k_6 + k_7 + k_8}{k_{10}} \cdot$$

$$\cdot \left[1 + \frac{k_4}{k_5 \cdot M} \cdot \frac{k_6 + k_7 + k_8}{k_6} \right] \cdot \frac{1}{TEB} \tag{32}$$

when acetone is photolysed in the presence of TEB, and $\phi_0(CO)$ is the quantum yield when acetone alone is photolysed at the same total pressure. Eqn. (32) will not hold if a reaction such as (33) is competing with reaction (30). The importance of reaction

$$CH_3CO^\cdot + TEB \rightarrow Et^\cdot + CH_3COBEt_2 \tag{33}$$
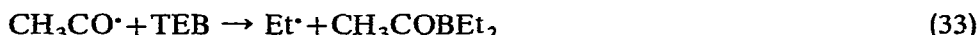
(33) can be evaluated from the effect of total pressure on $\phi(CO)$ and from a mass balance. The effect of total pressure on $\phi(CO)$ is shown in Fig. 4, where results obtained at constant light intensity and acetone and TEB pressures are shown as a function of total pressure, which was raised by adding different amounts of propane. From this figure it can be concluded that the effect of total pressure on $\phi(CO)$ is very small. This finding is compatible with the proposed mechanism as TEB is only able to react with thermalized triplets and an increase in total pressure would decrease the amount
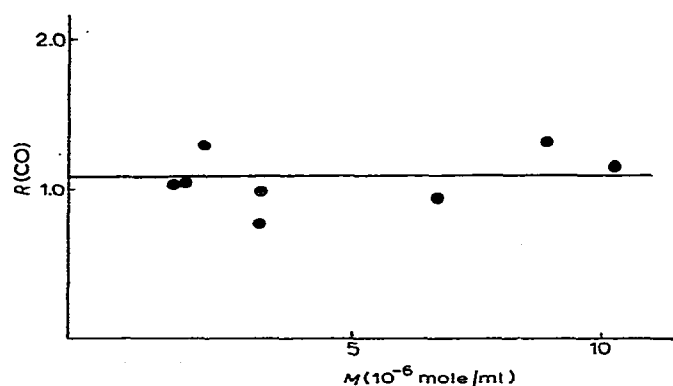

Fig. 4. Effect of total concentration in $R(CO)$ at constant TEB and acetone concentration and light intensity. Temp. 126°. [Acetone] 0.85×10^{-6} mole/ml; [TEB] 0.85×10^{-6} mole/ml. $R(CO)$ is given in 10^{-11} mole·ml^{-1}·s^{-1}. Propane added to increase the total concentration.

of acetyl radicals produced by reaction (4) but would increase the rate of reaction (6). These two effects would then tend to cancel out.

On the other hand, if there is no quenching of acetone triplets by TEB, the rate of acetyl radical production would be very slightly sensitive to the total pressure, as $\phi(CH_3CO^{\cdot})$ can be considered to be nearly unity under all conditions. Then relation 34 holds and $\phi(CO)$ should decrease noticeably when the total pressure decrease

$$\phi(CO) = k_{24}/(k_{24} + k_{27} \cdot [TEB]) \tag{34}$$

as reaction (30) is in the fall-off region[9]. We can conclude then that most of the decrease in carbon monoxide production must arise from reaction (10). The importance of reaction (30) can also be evaluated from a mass balance over the acetyl radicals. The number of acetyl radicals that did not react by reaction (30) can be evaluated from eqn. (35).

$$X = R(CH_3^{\cdot}) + R_{20} - 2 R(CO) \tag{35}$$

When the value of X thus obtained is related to the number W of ethyl radicals released for reactions other than reaction (20) it is found that W is much higher than

$$W = R(C_2H_5^{\cdot}) - R_{20} \tag{36}$$

X. This fact shows that most of the ethyl radicals must be produced by reaction (10).

That reaction (33) can be contributing to the diminution of carbon monoxide production cannot be completely disregarded as $2 \phi(CO)/\phi(CH_3)$ in the presence of TEB is slightly lower than that obtained in the photolysis of acetone alone.

Under conditions of low absorption, low conversion and constant light intensity, eqn. (37) will hold, where $R(CO)$ is the rate of carbon monoxide production

$$\frac{\phi(CO)}{\phi_0(CO) - \phi(CO)} = \frac{R(CO)}{R_0(CO) \cdot A/A_0 - R(CO)} \tag{37}$$

when acetone at concentration A is photolysed in the presence of a given concentration of TEB, and $R_0(CO)$ is the rate of production of carbon monoxide when pure acetone (concentration A_0) is photolysed at the same light intensity.

In Fig. 2 a plot of the left half of eqn. (37) against the inverse TEB concentration is given. The intercept of this plot has been estimated from the data obtained with 1,3-butadiene as quencher. The quasi independence of the $\phi(CO)$ on the 1,3-butadiene pressure shows that the thermal triplets are being quantitatively quenched[10]. The value found for $\phi(CO)/[\phi_0(CO) - \phi(CO)]$ can then be equated to $[k_4/(k_5 \cdot M)] \cdot (k_6 + k_7 + k_8)/k_6$. The value found (0.60) can be compared with the value previously reported[1] (0.37). The difference between these two values is very likely due to a difference in the average wavelength absorbed (see results obtained at 20°).

If the proposed mechanism is accepted, a value of

$$(k_6 + k_7 + k_8)/k_{10} = 5.9 \times 10^{-7} \text{ mole/ml}$$

can be derived from the slope and intercept of Fig. 2. From this value and previously reported data[1], it can be shown that

$$k_{10} = 3.4 \times 10^{11} \text{ ml} \cdot \text{mole}^{-1} \cdot \text{s}^{-1}$$

From the preceding discussion of the contribution of reaction (33) to the

decrease in carbon monoxide formation, it can be concluded that this value should be considered as an upper limit for k_{10}.

The similarity between the values obtained for k_{10} at 20 and $126°$ points to a very low activation energy for reaction (10). A similar result has been obtained for the quenching of biacetyl triplets by TEB[2]. The difference between the rate constant of reaction (10) at $20°$ and that found for the reaction of biacetyl triplets with TEB at the same temperature $(1.5 \times 10^{10}\ ml \cdot mole^{-1} \cdot s^{-1})$ can be partly due to differences in the preexponential A factors or to a difference of nearly 1 kcal/mole in the activation energies. This difference is well inside the estimated experimental errors.

Hydrogen abstraction from TEB

If the proposed set of reactions accounts for all the sources of methane, ethane, propane and butane, the rates of reactions (16) and (17) can be evaluated as

$$R_{17} + R_{19} = R(CH_4) - 0.04\ R(C_3H_8) \tag{38}$$

and

$$R_{16} + R_{18} = R(C_2H_6) - 0.13\ R(C_4H_{10}) - [R(C_3H_8)]^2 / 4\ R(C_4H_{10}) \tag{39}$$

It can then be shown that

$$\frac{R_{17} + R_{19}}{A \cdot (R_{13})^{\frac{1}{2}}} = \frac{k_{19}}{(k_{13})^{\frac{1}{2}}} + \frac{k_{17}}{(k_{13})^{\frac{1}{2}}} \cdot \frac{[TEB]}{A} \tag{40}$$

and

$$\frac{R_{16} + R_{18}}{A \cdot (R_{11})^{\frac{1}{2}}} = \frac{k_{18}}{(k_{11})^{\frac{1}{2}}} + \frac{k_{16}}{(k_{11})^{\frac{1}{2}}} \cdot \frac{[TEB]}{A} \tag{41}$$

By plotting the right halves of equations (40) and (41) against $[TEB]/A$, values of $k_{17}/(k_{13})^{\frac{1}{2}}$ and $k_{16}/(k_{11})^{\frac{1}{2}}$ can be obtained. These values are shown in Table 3. At $20°$ the intercept is higher than that expected from the low values of k_{18} and k_{19} at low temperatures. This fact can be due to some contribution to the rates of methane and ethane formation from reactions (42) and (43) respectively:

$$CH_3^- + CH_3CO^- \rightarrow CH_4 + CH_2CO \tag{42}$$

$$C_2H_5^- + CH_3CO^- \rightarrow C_2H_6 + CH_2CO \tag{43}$$

The contributions of these reactions is not significant at high $[TEB]/A$, where a rather high percentage of the radicals abstract hydrogen from TEB. Furthermore,

TABLE 3

HYDROGEN ABSTRACTION FROM TRIETHYLBORANE

Temp. (°C)	$k_{17}/k_{13}^{\frac{1}{2}}$ (mole$^{\frac{1}{2}} \cdot$ ml$^{-\frac{1}{2}} \cdot$ s$^{-\frac{1}{2}}$)	$k_{16}/k_{11}^{\frac{1}{2}}$ (mole$^{\frac{1}{2}} \cdot$ ml$^{-\frac{1}{2}} \cdot$ s$^{-\frac{1}{2}}$)
20	1.05 ± 0.35	0.65 ± 0.3
107	11.6 ± 4.0	5.5 ± 2.0
126	19 ± 5	15 ± 5

the method employed to evaluate k_{17} and k_{16} would minimize the error introduced by this extra source of methane and ethane.

The values obtained for k_{17} are in excellent agreement with those obtained in other systems[4] (azomethane/TEB, biacetyl/TEB and di-tert-butyl peroxide/TEB).

The values reported for k_{16}, even though they show a rather high dispersion, are in agreement with what can be expected from the relative reactivities of methyl and ethyl radicals towards the same substrate[11]. Furthermore, the relative values of k_{16}/k_{17} support the previously assumed ratio employed in previous publications[2,4] ($k_{16}/k_{17} = 0.5$).

The relatively high values found for k_{16} and k_{17} can be related to the weakness of the C–H bond α to the boron atom[4,12].

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