THE PHOTOOXIDATION OF CD$_3$N$_2$CD$_3$

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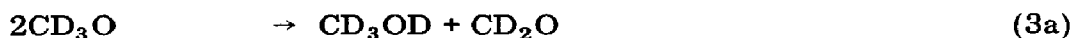(Received August 22, 1974; in revised form November 1, 1974)

Summary

The photooxidation of CD$_3$N$_2$CD$_3$ at 25 °C was studied, and the quantum yields of methanol, methylhydroperoxide, and dimethylperoxide were obtained. The fundamental variable of the system is $[O_2]/I_a^{1/2}$, where I_a is the absorbed intensity. The dimethylperoxide yield was invariant to a change of a factor of over 300 in this variable. However, the methanol yield dropped to a lower limiting value of 0.49 and the methylhydroperoxide yield rose to an upper limiting value of 0.38 as $[O_2]/I_a^{1/2}$ rose past 3000 (Torr-s)$^{1/2}$.

The results indicate that both the Raley *et al.* and Russell mechanisms are operative. The reactions between two CD$_3$O$_2$ radicals are:

$$2CD_3O_2 \;\; \rightarrow \;\; 2CD_3O + O_2 \tag{2a}$$

$$\rightarrow \;\; CD_3OD + CD_2O + O_2 \tag{2b}$$

$$\rightarrow \;\; CD_3O_2CD_3 + O_2 \tag{2c}$$

with reactions (2a), (2b), and (2c) occurring, respectively, 22, 60, and 18% of the time. There is no evidence for CD$_3$O$_2$CD$_3$ formation from CD$_3$O combination, and CD$_3$O is removed *via:*

$$2CD_3O \quad\qquad \rightarrow \;\; CD_3OD + CD_2O \tag{3a}$$

$$CD_3O + CD_3O_2 \;\; \rightarrow \;\; CD_3O_2D + CD_2O \tag{4}$$

$$CD_3O + O_2 \qquad \rightarrow \;\; CD_2O + DO_2 \tag{5}$$

with $k_4/(k_2 k_{3a})^{1/2} = 0.22$ and $k_5/k_{3a}^{1/2} = 7.1 \times 10^{-4}$ (Torr-s)$^{-1/2}$.

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Introduction

The subject of methyl radical oxidation has been of interest for some time. The major products are CH_3OH and CH_2O, and at room temperature in the gas phase the mechanism now generally accepted is that proposed by Raley *et al.* in 1951 [1]:
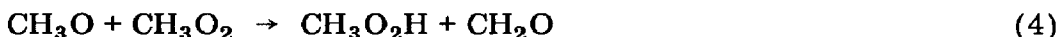
$$CH_3 + O_2 \; (+M) \rightarrow \; CH_3O_2 \; (+M) \tag{1}$$

$$2CH_3O_2 \qquad \rightarrow \; 2CH_3O + O_2 \tag{2a}$$

$$2CH_3O \qquad \rightarrow \; CH_3OH + CH_2O \tag{3a}$$

However, in 1957, Russell [2] proposed an alternate route to reaction (2a) to account for the same products:

$$2CH_3O_2 \; \rightarrow \; CH_3OH + CH_2O + O_2 \tag{2b}$$

Thus in the Russell scheme, CH_3O radicals would not be produced.

The Calvert group [3, 4] found CH_3O_2H as a product and introduced the additional step:

$$CH_3O + CH_3O_2 \; \rightarrow \; CH_3O_2H + CH_2O \tag{4}$$

This reaction, of course, requires that the mechanism of Raley *et al.* be operative, at least to some extent.

Two additional pieces of evidence to support the mechanism of Raley *et al.* came from the work of Heicklen and Johnston [5]. They used CH_3I photolysis as a source of CH_3 radicals and found CH_3OI as an initial product, which they felt confirmed the presence of CH_3O radicals in the system. Furthermore they found the CH_3O_2H quantum yield, $\Phi\{CH_3O_2H\}$, to increase with the ratio $[O_2]/I_a^{1/2}$ (I_a is the absorbed intensity), and proposed the steps:

$$CH_3O + O_2 \qquad \rightarrow \; CH_2O + HO_2 \tag{5}$$

$$CH_3O_2 + HO_2 \; \rightarrow \; CH_3O_2H + O_2 \tag{6}$$

Reaction (5) has since been shown to be important at room temperature [6].

Heicklen and Johnston also found $(CH_3O)_2$ as a product, but this could be produced with either the Raley *et al.* or Russell mechanisms by incorporating the following reactions, respectively:

$$2CH_3O \quad \rightarrow \; (CH_3O)_2 \tag{3b}$$

$$2CH_3O_2 \; \rightarrow \; (CH_3O)_2 + O_2 \tag{2c}$$

Unfortunately discrepancies now existed among the results, if the Russell mechanism is discarded. Heicklen and Johnston reported the ratio $[CH_3OH]/[(CH_3O)_2]$ to be between 9 and 12, but Dever and Calvert, working at much higher $[O_2]/I_a^{1/2}$, could not find $(CH_3O)_2$ and concluded that the ratio must exceed 60. Under the conditions of Dever and Calvert, reaction (3a) should have been negligible compared to reaction (5), and $\Phi\{(CH_3O)_2\}$ should have been close to zero. However, so should $\Phi\{CH_3OH\}$, but their

work, as well as the earlier work of Hanst and Calvert [7] under similar conditions, clearly demonstrated that CH_3OH was a major product.

The above problems suggest either that there is some error in the experimental observations or that the Raley *et al.* mechanism cannot, by itself, explain the results. Further evidence in support of the Russell mechanism was provided by Howard and Ingold [8] for s-butylperoxy radicals in the condensed phase below $-85\ °C$.

In order to check the experimental observations of Heicklen and Johnston, their work was repeated by Shortridge and Heicklen [9] using $CH_3N_2CH_3$ as a radical source rather than CH_3I. They used mass spectral detection and monitored CH_3O_2H and $(CH_3O)_2$ production. Their results generally agreed with those of Heicklen and Johnston.

If the Russell mechanism is not operative, then at high $[O_2]/I_a^{1/2}$, $\Phi\{CH_3OH\}$ and $\Phi\{(CH_3O)_2\}$ should approach zero and $\Phi\{CH_3O_2H\}$ should approach 1.0. However, under these conditions it is difficult to monitor CH_3OH and CH_3O_2H mass spectrometrically. In the case of methanol, its parent m/e is 32, the same as for O_2; for CH_3O_2H, its parent m/e is 48, the same as for O_3^+ produced in the mass spectrometer at high O_2 pressures. Thus Shortridge and Heicklen [9] were unable to extend their observations to high enough O_2 pressures to see if $\Phi\{CH_3O_2H\}$ really became 1.0.

In order to circumvent the experimental difficulties of Shortridge and Heicklen, we have now repeated the experiments using $CD_3N_2CD_3$ as a methyl radical source. In this way it is possible to monitor accurately both methanol and methylhydroperoxide at high O_2 pressures. The results of these experiments are reported here. They indicate that both the Russell and Raley *et al.* mechanisms are operative, and that most of the earlier results can be explained in a consistent way.

Experimental

The experimental apparatus and procedure are similar to those reported elsewhere [6]. Reaction mixtures were photolyzed in a 500 cm^3 Kimax cell using a Hanovia medium pressure Hg lamp. A Corning 0-52 filter was used for some of the low intensity experiments. The reaction gases exited continuously through a detachable pinhole into a differentially-pumped intermediate chamber maintained at a pressure $\leqslant 1$ Torr. These gases could then pass through a second leak which was permanently mounted on the mass filter of an Extranuclear quadrupole mass spectrometer type II. The pressure in the spectrometer was $\sim 3 \times 10^{-6}$ Torr for all experiments. Total gas pressure in the reaction cell was between 100 and 174 Torr, the higher pressures occurring when high O_2 concentrations were required.

The azomethame-d_6 (99% minimum isotopic purity) was obtained from Merck, Sharp, and Dohme of Canada Ltd. Mass spectral analysis confirmed that the isotopic purity was at least 95%. Gas chromatographic analysis showed $< 0.1\%$ of any chemical impurity. The O_2 and N_2 were Matheson extra dry and prepurified grades, respectively. Before use, the azomethane-d_6

was degassed at -130 °C, the O_2 was passed through two traps at -130 °C, and the N_2 was passed through two traps at -196 °C. The methanol (CH_3OH) used for calibration procedures was Baker analyzed spectrophotometric grade. It was assumed that the gas chromatographic sensitivity was the same for CH_3OH and CD_3OD.

Gas chromatographic analyses were performed on a Varian Aerograph 1520-B gas chromatograph employing a flame ionization detector. Methanol–azomethane separation was achieved on a 5 ft. × ¼in. o.d., stainless-steel column packed with Chromosorb 101 and operated at 90 °C with a helium carrier gas flow rate of 40 cm^3/min.

The value for the mass spectral sensitivity relative to the m/e 64 parent peak of azomethane-d_6 for the $CD_3O_2CD_3$ (m/e 68) product was assumed to be the same as its non-deuterated counterpart ($CH_3O_2CH_3$). This compound was synthesized as previously described [9] except that the reaction was run at 10 °C rather than 0 °C and only the fraction condensable at -23 °C was collected. The mass spectral sensitivity was determined to be 0.6 for $CH_3O_2CH_3$ (*i.e.* 0.6 Torr of $CH_3N_2CH_3$ gives the same mass spectral response at m/e 58 as 1.0 Torr of $CH_3O_2CH_3$ at m/e 62).

Owing to experimental difficulties, it was not possible to determine the mass spectral sensitivity for methanol directly. This sensitivity was obtained in an indirect manner by gas chromatographic analysis of reaction mixtures after photolysis. The relative gas chromatograph sensitivities were obtained using standard samples. This procedure yielded a value of 4.5 for the sensitivity of $CD_3OD(H)$ (m/e 35 + 36) peaks relative to the m/e 64 parent peak of $CD_3N_2CD_3$ [*i.e.* 4.5 Torr of $CD_3N_2CD_3$ gives the same response at m/e 64 as 1.0 Torr of $CD_3OD(H)$ gives at m/e 36 (35)] .

In order to generate quantum yields the m/e peak height ratios (35 + 36)/64, (51 + 52)/64 and 68/64 were plotted *versus* time. The 35 and 51 peaks must be included since H for D exchange involving CD_3OD and CD_3O_2D with the walls of the vessel occurs. The slopes of these plots yielded the rates of production of the $CD_3OD(H)$, $CD_3O_2D(H)$, and $CD_3O_2CD_3$ products, when corrected for the relative sensitivity calibration factors and multiplied by the pressure of azomethane. These product rates were converted to quantum yields by dividing by the N_2 production rate in separate actinometer experiments in the absence of O_2 but at the same $CD_3N_2CD_3$ pressure. For CD_3O_2D, mass spectral calibrations could not be made reproducibly, and only relative quantum yields were obtained.

Results

Quantum yields for methanol, methylhydroperoxide, and dimethyl-peroxide are given in Table 1 when 8.1 ± 0.1 Torr of $CD_3N_2CD_3$ was photo-oxidized at 25 °C. Since the CD_3OD and CD_3O_2D easily exchange D for H on the walls of the reaction vessel, the sum of the quantum yields for the OH and OD compounds are given. For CD_3OD (+ CD_3OH) and $CD_3O_2CD_3$, absolute quantum yields were obtained. For CD_3O_2D (+ CD_3O_2H), absolute

TABLE 1

Product quantum yields in the photooxidation of $CD_3N_2CD_3$ at 25 °C and $[CD_3N_2CD_3]$ = 8.1 ± 0.1 Torr [a]

$[O_2]/I_a^{1/2}$ (Torr-s)$^{1/2}$	$[O_2]$ (Torr)	$I_a \times 10^3$ (Torr/s)	$\Phi\{CD_3OD\}$ + $\Phi\{CD_3OH\}$	$\Phi\{CD_3O_2D\}$ + $\Phi\{CD_3O_2H\}$	$\Phi\{CD_3O_2CD_3\}$	$\Sigma\Phi\{x\}$ [b]
48	2.5	2.66	0.84	0.126	0.12	1.09
105	5.4	2.66	0.745	0.110	0.12	0.97
106	5.55	2.76	0.763	0.115	0.13	1.01
191	9.8	2.63	0.658	0.128	0.12	0.91
221	5.43	0.60	0.606	0.091	0.14	0.84
228	5.4	0.56	0.628	0.223	0.14	0.99
242	12.5	2.66	0.636	0.120	0.12	0.88
312	7.57	0.59	0.696	0.160	0.16	1.02
336	17.5	2.63	0.658	0.163	0.14	0.96
340	5.4	0.25	0.658	—	—	—
457	11.2	0.60	0.549	0.132	0.16	0.84
521	26.7	2.63	0.649	0.181	0.15	0.98
696	16.1	0.56	0.540	0.226	0.18	0.95
943	23.1	0.60	0.527	0.208	0.15	0.89
984	15.65	0.25	0.527	0.291	—	0.97
1124	26.0	0.56	0.529	0.271	0.20	1.00
1725	40.9	0.56	0.514	0.307	0.18	1.00
1740	42.3	0.59	0.591	0.280	0.15	1.02
2070	50.3	0.59	0.534	0.268	0.17	1.08
2116	23.0	0.115	0.464	—	—	—
2953	71.8	0.59	0.520	0.323	0.17	1.01
2980	47.4	0.25	0.471	0.414	0.11	1.00
3023	73.5	0.59	0.463	0.343	—	0.96
4058	93.9	0.56	0.468	0.259	—	0.88
4431	48.3	0.115	0.523	—	—	—
4885	118.7	0.59	0.479	0.411	—	1.04
5036	119.4	0.56	0.425	0.366	—	0.94
5880	92.9	0.25	0.460	0.360	—	0.97
6158	66.4	0.115	0.497	0.460	—	1.11
7715	121.9	0.25	0.384	0.342	—	0.87
9249	99.8	0.115	0.503	0.410	—	1.06
10500	113.3	0.115	0.527	0.458	—	1.14
12920	140.8	0.115	0.549	—	—	—
13610	148.3	0.115	0.482	—	—	—
15380	165.9	0.115	0.566	—	—	—

[a] Where possible, total pressure in all runs was approximately 100 Torr, which was obtained by adding N_2 where necessary.
[b] $\Sigma\Phi\{x\} \equiv \Phi\{CD_3OD\} + \Phi\{CD_3OH\} + \Phi\{CD_3O_2D\} + \Phi\{CD_3O_2H\} + \Phi\{CD_3O_2CD_3\}$. Where $\Phi\{CD_3O_2CD_3\}$ unavailable, it was assumed to be 0.15.

calibration was difficult and unreliable. Therefore the relative values were scaled so that for those runs with high CD_3O_2D yields, the average value of $\Phi\{CD_3O_2D\}$ + $\Phi\{CD_3O_2H\}$ satisfied the mass balance requirement:

$$\Sigma\Phi\{x\} = 1.0 \tag{I}$$

where

$$\Sigma\Phi\{x\} \equiv \Phi\{CD_3OD\} + \Phi\{CD_3OH\} + \Phi\{CD_3O_2D\} + \Phi\{CD_3O_2H\} +$$
$$\Phi\{CD_3O_2CD_3\}$$

The fundamental parameter of the system is $[O_2]/I_a^{1/2}$ and it was varied by a factor of 317. To do this $[O_2]$ was varied by a factor of 66; and I_a by a factor of 23. $\Phi\{CD_3OD\} + \Phi\{CD_3OH\}$ decreases and $\Phi\{CD_3O_2D\} + \Phi\{CD_3O_2H\}$ increases as $[O_2]/I_a^{1/2}$ is raised. $\Phi\{CD_3O_2CD_3\}$ remains fairly constant at about 0.15 ± 0.02.

Table 2 shows that changing the $CD_3N_2CD_3$ pressure or adding N_2 has no effect on $\Phi\{CD_3OD\} + \Phi\{CD_3OH\}$, and presumably also not on the other quantum yields.

The trends in the data for methanol and methylhydroperoxide are also shown more clearly in Fig. 1. The methanol yield exceeds 0.8 at $[O_2]/I_a^{1/2} < 100$ (Torr-s)$^{1/2}$ and drops to a lower limiting value of 0.49 as $[O_2]/I_a^{1/2}$ is raised to > 3000 (Torr-s)$^{1/2}$. The methylhydroperoxide yield has a lower limiting value of about 0.10 at $[O_2]/I_a^{1/2} < 100$ (Torr-s)$^{1/2}$ and rises to an upper limiting value of about 0.38 as $[O_2]/I_a^{1/2}$ rises above 3000 (Torr-s)$^{1/2}$.

Discussion

The fact that the methanol yield drops and the methylhydroperoxide yield increases with rising $[O_2]/I_a^{1/2}$ confirms the presence of CD_3O radicals and the importance of reaction (5). However, the Russell mechanism must also be operative since the methanol yield does not drop to zero.

Reactions (1) - (6) lead to the following steady-state expressions for the oxygenated radicals:

$$[CD_3O_2] = [(2I_a - R\{CD_3O_2D\} - R\{CD_3O_2H\})/2k_2]^{1/2} \tag{II}$$

$$[CD_3O] = [(k_{2a}/k_2)(2I_a - R\{CD_3O_2D\} - R\{CD_3O_2H\}) -$$
$$R\{CD_3O_2D\} - R\{CD_3O_2H\}]/2k_3 \tag{III}$$

where $R\{x\}$ indicates the rate of production of x. These expressions can be combined with the conservation of mass law:

$$\Phi\{CD_3O_2D\} + \Phi\{CD_3O_2H\} + \Phi\{CD_3OD\} + \Phi\{CD_3OH\} + \Phi\{CD_3O_2CD_3\}$$
$$= 1.0 \tag{IV}$$

to give the following rate laws based on the quantum yields of methanol and dimethyl peroxide:
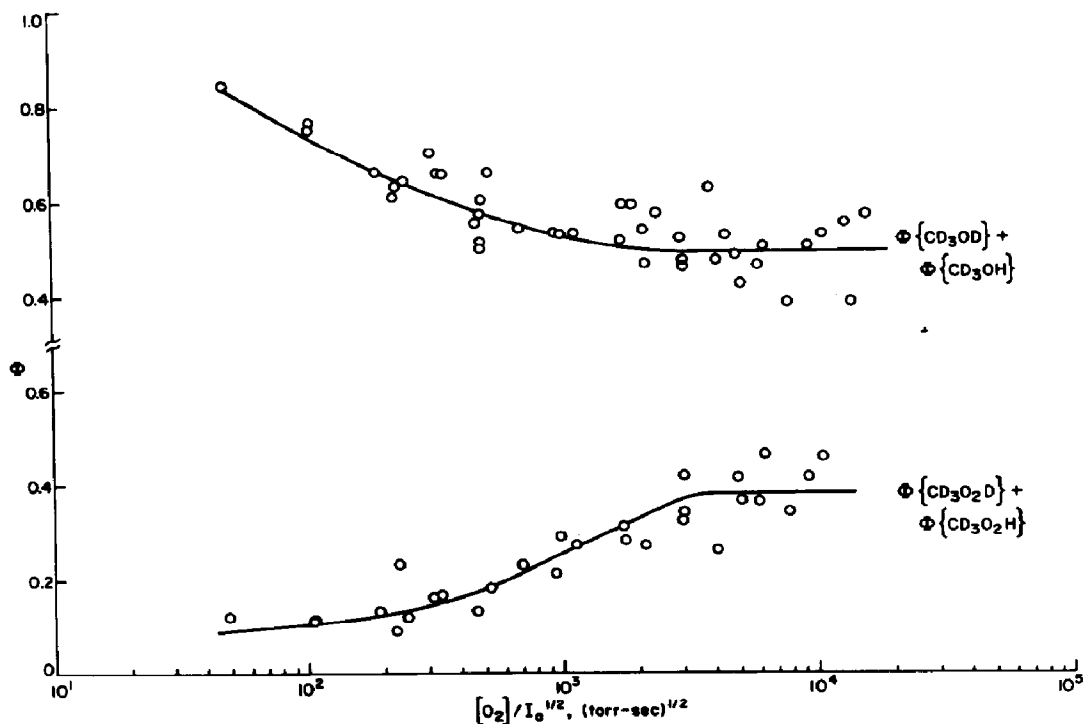
$$\frac{\Phi\{CD_3OD\} + \Phi\{CD_3OH\}}{A} = \frac{k_{2b}}{2k_2} + \frac{k_{3a}}{2k_3}\left(\frac{k_{2a}}{k_2} - \frac{B}{A}\right) \tag{V}$$

$$\frac{\Phi\{CD_3O_2CD_3\}}{A} = \frac{k_{2c}}{2k_2} + \frac{k_{3b}}{2k_3}\left(\frac{k_{2a}}{k_2} - \frac{B}{A}\right) \tag{VI}$$

TABLE 2

Effect of $CD_3N_2CD_3$ and N_2 pressure on the photooxidation of $CD_3N_2CD_3$

$[O_2]/I_a^{1/2}$ (Torr-s)$^{1/2}$	$[O_2]$ (Torr)	$I_a \times 10^3$ (Torr/s)	$[X]$ (Torr)	$\Phi\{CD_3OD\} + \Phi\{CD_3OH\}$
$X = CD_3N_2CD_3$				
479	6.0	0.157	2.1	0.51
1928	20.8	0.116	8.0	0.59
2366	41.5	0.307	20.0	0.57
3780	93.0	0.666	40.0	0.62
$X = N_2$, $[CD_3N_2CD_3] = 1.89 \pm 0.05$ Torr				
488	6.15	0.159	0	0.57
488	6.11	0.158	81	0.50
488	6.20	0.162	645	0.60

Fig. 1. Semilog plots of the quantum yields of methanol and methylhydroperoxide vs. $[O_2]/I_a^{1/2}$ in the photooxidation of $CD_3N_2CD_3$ at 25 °C.

where

$$A \equiv 1 + \Phi\{CD_3OD\} + \Phi\{CD_3OH\} + \Phi\{CD_3O_2CD_3\}$$

$$B \equiv 1 - \Phi\{CD_3OD\} - \Phi\{CD_3OH\} - \Phi\{CD_3O_2CD_3\}$$

At high $[O_2]/I_a^{1/2}$, all the quantum yields become constant and $k_{2a}/k_2 = B/A$.
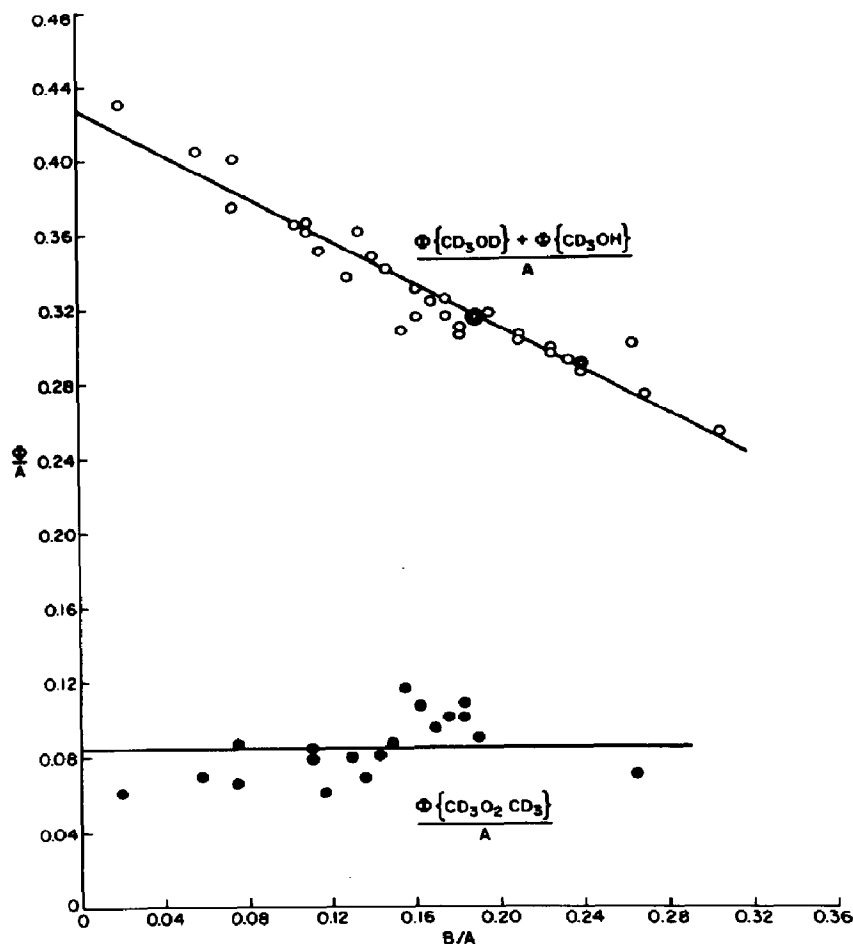
Fig. 2. Plots of $(\Phi\{CD_3OD\} + \Phi\{CD_3OH\})/A$ and $\Phi\{CD_3O_2CD_3\}/A$ *vs.* B/A in the photolysis of $CD_3N_2CD_3$ at 25 °C. $A \equiv 1 + \Phi\{CD_3OD\} + \Phi\{CD_3OH\} + \Phi\{CD_3O_2CD_3\}$; $B \equiv 1 - \Phi\{CD_3OD\} - \Phi\{CD_3OH\} - \Phi\{CD_3O_2CD_3\}$.

The value of B/A, and thus k_{2a}/k_2, is 0.22 under these conditions. Likewise, under these conditions, if eqn. (V) is divided by eqn. (VI), then the ratio of the methanol yield to the dimethylperoxide yield, which is 3.26, gives k_{2b}/k_{2c}. The fraction of reaction (2) going by channels (2a), (2b) and (2c) is 0.22, 0.60 and 0.18, respectively.

Figure 2 shows plots of the left-hand sides of eqns. (V) and (VI) *vs.* B/A. The upper plot has a slope of —0.58, which gives k_{3a}/k_3 = 1.16. Of course the possible upper limit for k_{3a}/k_3 = 1.0, so that the larger-than-possible value reflects the experimental uncertainty. The intercept gives $k_{2b}/2k_2 + k_{2a}k_{3a}/2k_2k_3$ = 0.43 in exact agreement with the value computed from the already evaluated rate coefficient ratios.

The lower plot in Fig. 2 seems to show a slightly positive slope, a condition which is impossible since it leads to negative rate coefficients. However, the data can be reasonably well fitted with a horizontal line at 0.084, and this has been done. The zero slope corresponds to k_{3b}/k_3. The

intercept of 0.084 corresponds to $k_{2c}/2k_2 + k_{2a}k_{3b}/2k_2k_3$ and it agrees reasonably well with the value of 0.091 calculated from the already evaluated rate coefficient ratios.

From the methylhydroperoxide yield the following rate law is obtained:

$$\frac{\Phi\{CD_3O_2D\} + \Phi\{CD_3O_2H\}}{C^{1/2}(Ck_{2a}/k_2 - \Phi\{CD_3O_2D\} - \Phi\{CD_3O_2H\})^{1/2}}$$

$$= \frac{k_4}{2(k_2k_3)^{1/2}} + \frac{k_5[O_2]}{(2k_3)^{1/2}(CI_a)^{1/2}}$$

(VII)

where

$$C \equiv 2 - \Phi\{CD_3O_2D\} - \Phi\{CD_3O_2H\}$$

Figure 3 gives a plot of the left-hand side of eqn. (VII) $vs.$ $[O_2]/(CI_a)^{1/2}$. The data are quite scattered, but the best straight line gives a slope of 5.0×10^{-4} $(\text{Torr-s})^{-1/2}$ and an intercept of 0.11. The former number corresponds to $k_5/(2k_3)^{1/2}$, whereas the latter number corresponds to $k_4/2(k_2k_3)^{1/2}$.

We now re-analyze the earlier data on CH_3 oxidation. If we ignore the data on CH_3OH yields, which seems most unreliable, then the two rate laws of pertinence are:

$$\frac{\Phi\{CH_3O_2CH_3\}}{\alpha - \Phi\{CH_3O_2H\}} = \frac{k_{2c}}{2k_2} + \frac{k_{3b}}{2k_3}\left[\frac{k_{2a}}{k_2} - \frac{\Phi\{CH_3O_2H\}}{\alpha - \Phi\{CH_3O_2H\}}\right]$$

(VIII)

$$\frac{\Phi\{CH_3O_2H\}}{(\alpha - \Phi\{CH_3O_2H\})^{1/2}[(k_{2a}/k_2)(\alpha - \Phi\{CH_3O_2H\}) - \Phi\{CH_3O_2H\}]^{1/2}}$$

$$= \frac{k_4}{2(k_2k_3)^{1/2}} + \frac{k_5}{(2k_3)^{1/2}}\frac{[O_2]}{I_a^{1/2}(\alpha - \Phi\{CH_3O_2H\})^{1/2}}$$

(IX)

where $\alpha = 2$ when $CH_3N_2CH_3$ photolysis is the source of CH_3, and $\alpha = 1$ when CH_3I photolysis is the source of CH_3.

From the data of Shortridge and Heicklen [9], who used $CH_3N_2CH_3$ as a CH_3 source, the upper limiting value for $\Phi\{CH_3O_2H\}$ was about 0.60. Thus $k_{2a}/k_2 = 0.43$.

Figure 4 is a plot of $\Phi\{CH_3O_2CH_3\}/(\alpha - \Phi\{CH_3O_2H\})$ $vs.$ $\Phi\{CH_3O_2H\}/(\alpha - \Phi\{CH_3O_2H\})$. There is no trend in the data, and the slope gives $k_{3b}/k_3 = 0$. The intercept gives $k_{2c}/2k_2 = 0.036$.

Figure 5 is a plot of the left-hand side of eqn. (IX) $vs.$ $[O_2]/I_a^{1/2} \times (\alpha - \Phi\{CH_3O_2H\})^{1/2}$. The data are quite scattered, and those of Heicklen and Johnston lie below those of Shortridge and Heicklen, probably reflecting errors in mass spectrometer calibrations. However, there is a trend in the data and there is a positive intercept. The data are fitted with a line of slope 3.3×10^{-4} $(\text{Torr-s})^{-1/2}$ and an intercept of 0.10, corresponding respectively to $k_5/(2k_3)^{1/2}$ and $k_4/2(k_2k_3)^{1/2}$.
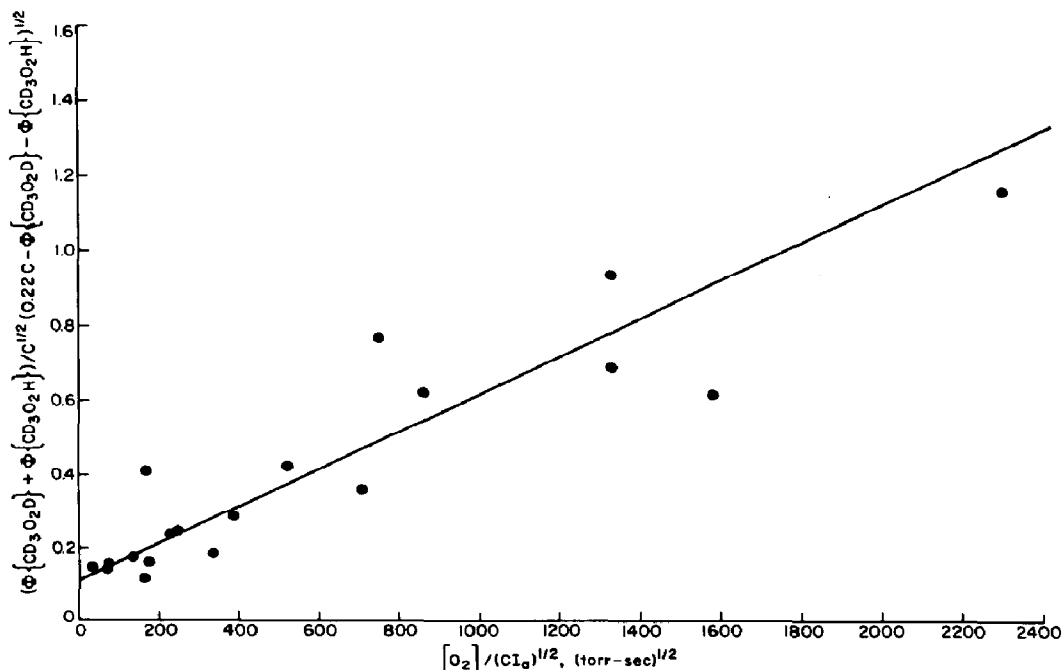
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Fig. 3. Plot of $(\Phi\{CD_3O_2D\} + \Phi\{CD_3O_2H\})/C^{1/2} (0.22C - \Phi\{CD_3O_2D\} - \Phi\{CD_3O_2H\})^{1/2}$ vs. $[O_2]/(CI_a)^{1/2}$ in the photooxidation of $CD_3N_2CD_3$ at 25 °C. $C \equiv \alpha - \Phi\{CD_3O_2D\} - \Phi\{CD_3O_2H\}$.
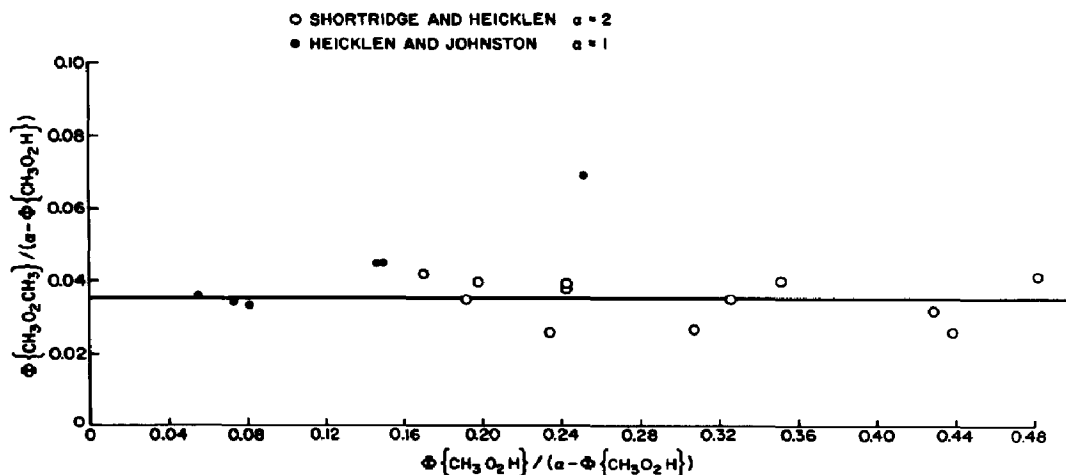
Fig. 4. Plot of $\Phi\{CH_3O_2CH_3\}/(\alpha - \Phi\{CH_3O_2H\})$ vs. $\Phi\{CH_3O_2H\}/(\alpha - \Phi\{CH_3O_2H\})$ in the room temperature (25 °C) photooxidation of CH_3I (data of Heicklen and Johnston [5], $\alpha = 1$) and $CH_3N_2CH_3$ (data of Shortridge and Heicklen [9], $\alpha = 2$).

The rate coefficient ratios are summarized in Table 3. For both CD_3 and CH_3, the Russell mechanism accounts for more than ½ the oxidation. There appears to be a large isotope effect on the ratio k_{2a}/k_{2c}, so large that it is difficult to believe. Possibly it reflects calibration inaccuracies for dimethylperoxide and methylhydroperoxide.
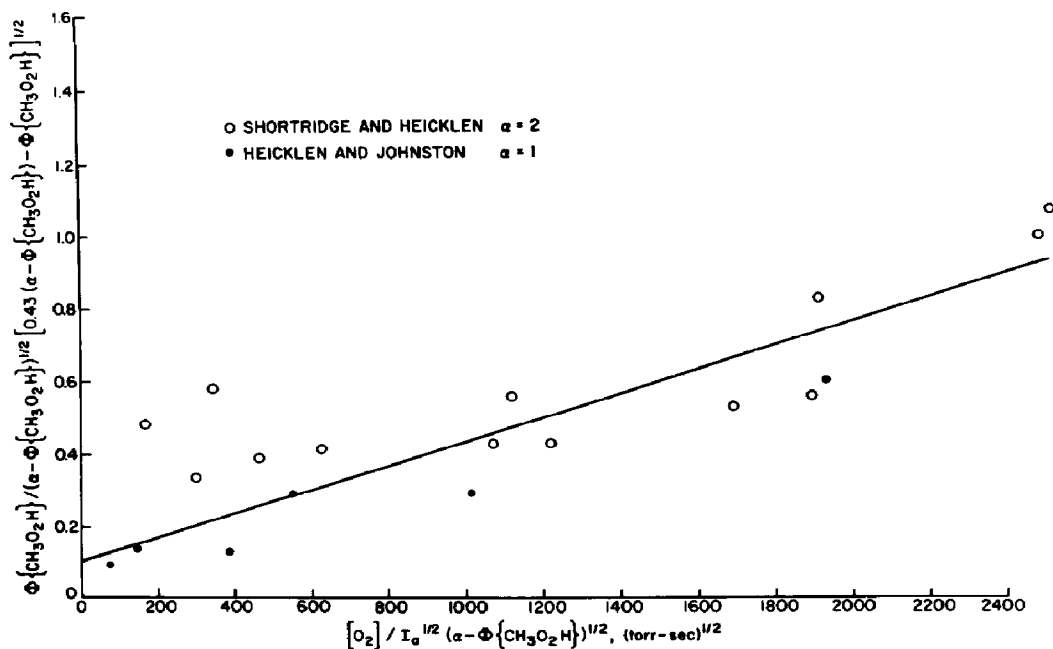
Fig. 5. Plot of $\Phi\{CH_3O_2H\}/(\alpha - \Phi\{CH_3O_2H\})^{\frac{1}{2}}$ $[0.43(\alpha - \Phi\{CH_3O_2H\}) - \Phi\{CH_3O_2H\}]^{\frac{1}{2}}$ vs. $[O_2]/I_a^{\frac{1}{2}}$ $(\alpha - \Phi\{CH_3O_2H\})^{\frac{1}{2}}$ in the room temperature (25 °C) photooxidation of CH_3I (data of Heicklen and Johnston [5], $\alpha = 1$) and $CH_3N_2CH_3$ (data of Shortridge and Heicklen [9], $\alpha = 2$).

TABLE 3

Summary of rate coefficient ratios at 25 °C

Ratio	Units	Value	
		CD_3	CH_3
k_{2a}/k_2	None	0.22	0.43
k_{2b}/k_2	None	0.60	0.50
k_{2c}/k_2	None	0.18	0.072
k_{3a}/k_3	None	1.0	1.0
k_{3b}/k_3	None	0.0	0.0
$k_4/(k_2k_3)^{\frac{1}{2}}$	None	0.22	0.20
$k_5/k_3^{\frac{1}{2}}$	$(Torr\text{-}s)^{-\frac{1}{2}}$	7.1×10^{-4}	4.6×10^{-4}

Another surprising feature is that k_{3b}/k_3 is negligibly small, and that essentially all the peroxide comes through the Russell mechanism.

The value of k_5 can be estimated from the reported value [10] of $k_3 = 6 \times 10^9$ - 4×10^{10} M^{-1} s^{-1} and the value of $\sim 4.6 \times 10^{-4}$ $(Torr\text{-}s)^{-\frac{1}{2}}$ found here for $k_5/k_3^{\frac{1}{2}}$. The estimated value of k_5 becomes $\sim (4.8$ - $12.5) \times 10^3$ M^{-1} s^{-1} in reasonable agreement with the deduced value [10] of $\sim 2 \times 10^3$ M^{-1} s^{-1} at 25 °C.

Of course, some small amount of dimethylperoxide must be produced

from reaction (3b), since its reverse is known to occur. In fact if we take $k_{3a} = 4 \times 10^{10} \, M^{-1} \, s^{-1}$ (the upper limit of the available data [10]), and combine that with the estimated value [10] for k_{3b}, then $k_{3a}/k_{3b} \sim 70$, which would make reaction (3b) undetectable in our system. However, since essentially all of the $CH_3O_2CH_3$ appears to be produced through the Russell mechanism, it is not clear why it was not detected by Calvert and his coworkers.

Acknowledgement

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