THE REACTION OF METHYL RADICALS WITH OXYGEN AND COMPARISON WITH OTHER THIRD-ORDER REACTIONS

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At 200° C, methyl radicals are shown to react with oxygen according to the reaction

$$CH_3 + O_2 + M = CH_3OO + M.$$

Experimental evidence is presented to show that this reaction is third-order at pressures up to at least 200 mm of acetone; and has a rate constant, at 200° C and when M is the acetone molecule, of $1{\cdot}6 \times 10^{-31}$ (cm^3/molecule)^2 sec^{-1}. The CO_2 molecule is approximately 0·1 times as efficient a third body as the acetone molecule. The conclusion that the reaction is third order under the stated conditions and the order of magnitude of the rate constant deduced are in accord with theoretical expectations and comparison with the reactions $H + O_2 + M = HO_2 + M$ and $CH_3 + CH_3 + M = C_2H_6 + M$. The reaction $CH_3 + NO + M = CH_3NO$ is also third order, at least at pressures around 0·2 mm of di-*tert*.-butyl peroxide.

It is a striking fact that, although the methyl radical and the oxygen molecule are comparatively simple entities, there is as yet no certainty as to the nature of the reaction that occurs between them. This paper records and discusses experiments to determine the order and rate constant of the reaction. We shall see that the results have a unique implication as to the reaction products.

EXPERIMENTAL

The experiments consisted of a study of the photolysis of acetone in the presence of small quantities of oxygen, with and without the addition of large quantities of inert gas (carbon dioxide). Apart from the inert gas work, the method was essentially that used earlier by Marcotte and Noyes.[1]

The apparatus and the methods used for the preparation of materials and the analysis of products were similar to those previously described.[2] A beam of light, effectively limited to the wavelengths 3130 and 3020 Å, filled a silica reaction cell of 2·8 cm diam. and 20 cm length. The cell was placed in the centre position of a furnace, controlled by a Sunvic R.T.2 controller, and was at 200° C except at the extreme ends where a drop of about 1° C occurred. The absorbed light intensity, with 200 mm of acetone present, was $1{\cdot}05 \times 10^{13}$ quanta cm^{-3} sec^{-1} and, with 10 mm, was $1{\cdot}05 \times 10^{12}$ quanta cm^{-3} sec^{-1}. The oxygen pressure was kept constant, as consumption took place, by the addition of small doses. A magnetically operated stirrer kept the gases mixed during the reaction, but it was found necessary when using the higher pressures to allow time for the oxygen doses to mix thoroughly with the gases already in the cell, by cutting off the light with a screen immediately before each addition. Quantum yields were calculated by comparison with the yield of carbon monoxide from the photolysis of acetone which has a quantum yield of unity. Since added carbon dioxide increases the absorbed light intensity,[3] quantum yields for the photo-oxidation of acetone in the presence of carbon dioxide were calculated by comparison with the carbon monoxide produced in the same gas mixtures but with the oxygen omitted.

RESULTS

It can be assumed that, at 200° C with pressures of oxygen less than 0·5 mm, the photolysis of acetone gives effectively two methyl radicals and a carbon monoxide molecule.[4]

The quantum yield of methane has been shown by Marcotte and Noyes [1, 4] to be decreased by the addition of amounts of oxygen between 10^{-1} and 10^{-2} mm pressure. Marcotte and Noyes plausibly attribute this to a competition between two reactions; the methyl radical may react either with oxygen or with acetone, only the latter reaction leading to methane production. Accepting this, we may write the following equations:

$$CH_3COCH_3 + h\nu = 2CH_3 + CO \tag{1}$$

$$CH_3 + CH_3COCH_3 = CH_4 + CH_3COCH_2 \tag{2}$$

$$CH_3 + O_2 = \quad ? \tag{3}$$

$$CH_3 + CH_3 = C_2H_6 \tag{4}$$

Assuming that methane arises only as shown in reaction (2) and that no other reaction of CH_3 radicals occurs, we can deduce that

$$\frac{2 - \phi_{CH_4} - 2\phi_{C_2H_6}}{\phi_{CH_4}} = \frac{k_3[O_2]}{k_2\,[\text{acetone}]}, \tag{5}$$

where ϕ stands for the quantum yield. In practice, the yield of ethane was negligible except at the lower acetone and oxygen pressures. If, at the pressures used, reaction (3) is second order as written, the quantity (R) on the left-hand side of eqn. (5), multiplied by the ratio of the acetone to oxygen pressure should be constant. If, on the other hand, reaction (3) is third order (i.e. first order with respect to concentration of a third body M), then since in the absence of added inert gas M is effectively acetone, eqn. (5) reduces to

$$\frac{2 - \phi_{CH_4} - 2\phi_{C_2H_6}}{\phi_{CH_4}} = \frac{k_3[O_2]}{k_2}. \tag{6}$$

In that case, division of R by the corresponding oxygen pressure should give a constant (k_3/k_2) no matter what the oxygen pressure. It can be seen from the first part of table 1 that $R/[O_2]$ is much more nearly constant than $R \times [\text{acetone}]/[O_2]$. It appears therefore that, between pressures of 30 and 200 mm of acetone, reaction (3) is third, and not second, order, and should be written

$$CH_3 + O_2 + M = CH_3OO + M. \tag{3'}$$

It is true that there is a tendency for a decreased value of k_3/k_2 at low oxygen pressures; but this is probably due to irregularities in the oxygen pressure occasioned by insufficient mixing. In table 1 the data for 131 mm of acetone are taken from the results of Marcotte and Noyes.[1]

The average value of k_3/k_2 at 200° C of $2{\cdot}5 \times 10^{-15}$ cm/molecule can be combined with the value [5] for $k_2/(k_4)^{\frac{1}{2}}$ at 200° C of $3{\cdot}2 \times 10^{-12}$ $(\text{cm}^3/\text{molecule})^{\frac{1}{2}}\ \text{sec}^{-\frac{1}{2}}$ to obtain a value of 8×10^{-27} $(\text{cm}^3/\text{molecule})^{\frac{3}{2}}\ \text{sec}^{-\frac{1}{2}}$ for $k_3/(k_4)^{\frac{1}{2}}$ at 200° C. Hence, if the collision number, steric factor and activation energy for reaction (4) are taken as $4{\cdot}2 \times 10^{-10}$ $(\text{cm}^3/\text{molecule})\ \text{sec}^{-1}$, unity and zero respectively, we obtain $k_3 = 1{\cdot}6 \times 10^{-31}$ $(\text{cm}^3/\text{molecule})^2\ \text{sec}^{-1}$ at 200° C and when M is acetone.

The second part of table 1 shows that, at a very low acetone pressure, R is greater than expected. In other words, at low pressures, the yield of methane and ethane is less than expected. One way of explaining this would be to suppose an increase in the importance of a second-order reaction between CH_3 and O_2 at these low pressures:

$$CH_3 + O_2 = CH_3OO^* \overset{k_7}{=} \text{decomposition products.} \tag{7}$$

The idea is that, at very low pressures, the energy-rich CH_3OO radical may decompose into oxidation products instead of simply being deactivated or dissociating into a CH_3 radical and O_2 molecule. If this happened, the combined rate of reaction of CH_3 radicals with O_2 molecules would be $\frac{(k_7 + k_C[M])k_A}{k_7 + k_B + k_C[M]}$, where k_A, k_B, k_C refer respectively to the steps

$$CH_3 + O_2 = CH_3OO^* \tag{A}$$

$$CH_3OO^* = CH_3 + O_2 \tag{B}$$

$$CH_3OO^* + M = CH_3OO + M, \tag{C}$$

which together can be considered to make up reaction (3′). If $k_B \gg k_7 + k_C[M]$, but k_7 is only negligible in comparison with $k_C[M]$ at acetone pressures above 10 mm (or with large inert gas pressures), the rate of reaction of CH_3 radicals and O_2 molecules would be that expected from reaction (3′) at high acetone pressures, but greater than that expected from reaction (3′) at an acetone pressure of 10 mm.

In the presence of added inert gas, the rate of reaction (3′) should be increased and therefore the methane yield should be reduced. As shown in the third part of table 1, addition of up to 280 mm of carbon dioxide to 10 mm of acetone increased the apparent value of k_3/k_2 by a factor of *ca.* 2. This increase provides strong, independent, evidence that, under the conditions used, reaction (3) has a total order of three, including first order dependence on the concentration of a third body which can be an inert gas. Making due allowance for the above-noted fall in the methane yield (increase in k_3/k_2) at low pressures, it may be calculated that carbon dioxide is approximately 0·1 times as efficient a third body in reaction (3′) as acetone. Dodd and Steacie [6] found carbon dioxide to be 0·03 times as efficient a third body as acetone for the combination of two methyl radicals.

TABLE 1

acetone mm	oxygen mm × 10^3	CO_2 mm	R	$R/[O_2]$ mm^{-1}	$R \times \frac{[\text{acetone}]}{[O_2]}$
(i) 200	917	0	55·2	60	12,000
200	424	0	23·4	55	11,000
200	181	0	8·3	46	9,200
200	65·5	0	2·56	39	7,800
131	165	0	7·70	47	6,160
131	98	0	6·14	63	8,260
131	74	0	3·66	50	6,550
131	53	0	2·28	43	5,640
131	43	0	1·70	40	5,240
131	38	0	1·50	40	5,240
30	542	0	28·9	53	1,590
30	216	0	14·7	68	2,040
30	147	0	6·9	47	1,410
30	116	0	4·3	37	1,110
(ii) 10	157	0	16·7	107	1,070
10	92	0	12·7	138	1,380
10	65·5	0	7·2	110	1,110
10	62·5	0	6·7	107	1,070
10	49	0	5·1	104	1,040
10	38·5	0	3·2	83	830
(iii) 10	93	20	11·2	120	1,200
10	84	90	12·6	150	1,500
10	142	271	30·0	211	2,110
10	91	278	25·4	279	2,790
10	78	280	17·3	222	2,220
10	43	274	8·4	195	1,950
10	33·5	280	12·7	379	3,790

DISCUSSION

THE PRODUCTS OF THE REACTION

The finding that, at 200° C and at pressures up to at least 200 mm of acetone, the reaction of methyl radicals with oxygen has a total order of three (including first-order dependence on the concentration of a third body, which can be an inert gas) can only mean that under the conditions used the reaction products are CH_3OO radicals, i.e. that the reaction must be written as (3′).

That at temperatures from 0° C to at least 200° C the products are CH_3OO radicals was previously probable—as Blaedel, Ogg and Leighton [7] and Raley, Porter, Rust and Vaughan [8] first argued—from the fact that at such temperatures it is well established that the reaction of methyl radicals with oxygen ultimately produces considerable quantities of methyl alcohol.[9, 7, 8, 10, 11] Any first step other than (3′) that would not need a high activation energy, such as

$$CH_3 + O_2 = HCHO + OH \qquad (8$$

or

$$CH_3 + O_2 = HCO + H_2O \qquad (9)$$

leads to no plausible reaction forming methyl alcohol. The present work provides a strong and more direct argument that the first step is correctly written as (3′) and not, e.g., as (8) or (9).

THE ORDER OF THE REACTION

That it was previously probable that the reaction produced CH_3OO radicals implied that the reaction, in its overall form, was termolecular (as (3′)), but left open the question whether the termolecular reaction was second or third order at the pressures, and in the presence of the particular third-body gases, used in the experimental work thus far. At sufficiently low pressures (3′) should be third order; at sufficiently high pressures the rate should be second order and independent of the concentration of M.

All previous workers have taken the reaction as second order under the relevant experimental conditions. The justification for doing this has lain exclusively in the experimental work of Bates and Spence.[9] Two arguments have been employed. Bates and Spence photolyzed methyl iodide in the presence of oxygen. Under their conditions, the reaction of methyl radicals with oxygen competed with some reaction re-forming methyl iodide. The latter reaction was taken to be

$$CH_3 + I_2 = CH_3I + I. \qquad (10)$$

It was argued that the former reaction (taken as (8)) must be second order because the addition of 40 mm nitrogen to a mixture of 50 mm methyl iodide + 10 mm oxygen made no significant difference to their results. This evidence is not strong, for it would be quite possible (see ref. (15)) for the efficiency of methyl iodide molecules as third bodies in bringing about reaction (3′), when third order, to be much greater than the efficiency of nitrogen molecules. In that case only 40 mm nitrogen would have little effect when added to the above mixture. The second argument is due to Blaedel *et al.*[7] They claim that the results of Bates and Spence show that, as the total pressure of a methyl iodide + oxygen mixture is varied over an " eight-fold " range, the ratio of the rate constant of the reaction re-forming methyl iodide to the rate constant of the reaction between methyl radicals and oxygen remains constant. If, therefore, the former reaction is second order, so must be the latter. This evidence is also not compelling. In the first place, it is not certain that the reaction re-forming methyl iodide, under the conditions used by Bates and Spence, was the second-order reaction (10) and not the third-order reaction

$$CH_3 + I + M = CH_3I + M. \qquad (11)$$

In the second place, Blaedel *et al.* have over-stated the evidence to be found in the results of Bates and Spence for the constancy of the ratio of rate constants. In fact, only a few experiments were performed with low enough oxygen pressures for the rate of (10) to be comparable with the rate of (8) or (3′). In the rest of the experiments, the rate of reaction (10) was small or negligible in comparison with the rate of (8) or (3′). Consequently, in effect the theory is based on a two-fold not an eight-fold change. The present work provides strong evidence that, under the conditions used, (3′) is of third and not of second order.

THE RATE CONSTANT OF THE REACTION

There have been previous estimates of the rate constant of the reaction between CH_3 radicals and oxygen, all based upon the supposition that the reaction was second order. Marcotte and Noyes[1] compared the rate at which CH_3 radicals, produced by the photolysis of 131 mm of acetone at 120 to 200° C, reacted with small quantities of oxygen and the rate at which CH_3 radicals reacted with acetone to give methane. Knowledge of the rate of the latter reaction enabled Marcotte and Noyes to deduce that (i) the activation energy of the reaction of CH_3 radicals with oxygen is close to zero (ii) if the reaction of CH_3 radicals with oxygen is taken as second order (irrespective of its products, though these were actually formulated as in (9)), its steric factor must be low and *ca.* $2 \times 10^{-4} \times$ the square root of the steric factor for the second-order combination of two CH_3 radicals. Various corrections to the data have subsequently led [12] to the figure of 2×10^{-4} being revised to *ca.* 4×10^{-4}.

The second order combination of two CH_3 radicals is known to have a steric factor close to unity,[6] as has also the second-order association of two *n*-propyl radicals.[13] In any case, however, if the reaction of CH_3 radicals with oxygen *is* taken as second order, the steric factor is surprisingly low in relation to that of the second-order association of two CH_3 radicals to give ethane. In view of the evidence given that the reaction of CH_3 radicals with oxygen is also an association (as formulated in (3′)), there appears to be no reason why the steric factor of the latter reaction should be so much less than the steric factor of the alkyl radical associations. Essentially, conclusion (ii) of Marcotte and Noyes means that the rate of reaction of CH_3 radicals with oxygen is much less than would be expected for reaction (3) if second order. The present work shows that there is no need to interpret the slowness by a surprisingly low steric factor for an assumed second-order reaction; the slowness is due to the reaction being third order under the conditions used. Assuming a collision number of $4{\cdot}2 \times 10^{-10}$ (cm^3/molecule) sec^{-1} for methyl radicals colliding with oxygen molecules and a steric factor of 4×10^{-4}, division of the second-order rate constant by the acetone concentration (equivalent to 131 mm Hg) gives a third-order rate constant of $0{\cdot}7 \times 10^{-31}$ (cm^3/molecule)^2 sec^{-1}.

Hoey and Kutschke [10] compared the rate at which CH_3 radicals reacted with small quantities of oxygen and the rate at which CH_3 radicals reacted with azomethane to give methane. They produced CH_3 radicals by the photolysis of 101 mm of azomethane at temperatures from 123° C to 161° C. They too supposed the reaction of CH_3 radicals with oxygen to be second order and deduced that the reaction had a negligible activation energy and a steric factor $\sim 7 \times 10^{-3}$. If, however, the reaction is taken as (3′) and as third order under the conditions used, the third-order rate constant at 160° C when M is azomethane works out to be $1{\cdot}3 \times 10^{-30}$ (cm^3/molecule)^2 sec^{-1}. In deducing this we have taken the same collision number as assumed above for the collision of CH_3 radicals with O_2 molecules.

Ingold and Bryce,[14] using the pyrolysis of mercury dimethyl as a source of CH_3 radicals, found that, at an oxygen pressure of 0·02 mm and in the presence of a large excess (10 mm) of helium, one in 10^3 or 10^4 collisions of CH_3 radicals with O_2 molecules was effective in bringing about reaction at 1000°C. Assuming that reaction (3′) was the only reaction occurring between CH_3 radicals and O_2 molecules and that this reaction was third order, the estimated collision efficiency implies a rate constant for (3′), when M is helium, between 9×10^{-30} and 9×10^{-31} (cm^3/molecule)^2 sec^{-1} at 1000° C. In deducing these figures, we have assumed a collision number equal to *ca.* $6{\cdot}7 \times 10^{-10}$ (cm^3/molecule) sec^{-1} for collision of CH_3 radicals with O_2 molecules at 1000° C; this number is in accord with that assumed for 200° C.

The probability is that the azomethane molecule, like the acetone molecule, is of almost perfect efficiency in bringing about reaction (3′).[15] The helium molecule has probably a lower efficiency. The three earlier quantitative estimates of the rate of reaction of CH_3 radicals and O_2 molecules are thus not in good agreement, whether the reaction is taken to be of second or of third order. However, they all agree qualitatively in saying that the reaction is slow; and in view of the difficulty of explaining the slowness other than by assuming a third order reaction, may be said qualitatively to support our own direct evidence that the reaction is third order under the conditions used.

Quantitatively, our own results are in good agreement with those of Marcotte and Noyes; though the more extensive data of the first part of table 1 lead to a third-order rate constant rather greater than that deduced above from the data of Marcotte and Noyes alone, viz. $1\cdot6 \times 10^{-31}$ (cm^3/molecule)^2 sec^{-1} at 200° C and when M is acetone.

COMPARISON WITH THE ORDERS AND RATE CONSTANTS OF OTHER TERMOLECULAR REACTIONS

THE COMBINATION OF ATOMS AND THE REACTIONS

$$H + O_2 + M = HO_2 + M, \quad CH_3 + CH_3 + M = C_2H_6 + M.$$

Most combinations of two particles X and Y may be considered to involve the three reactions

$$X + Y = XY^* \tag{A}$$

$$XY^* = X + Y \tag{B}$$

$$XY^* + M = XY + M. \tag{C}$$

Taken together, these three reactions lead to the expression

$$(k_A k_C[X][Y][M]/(k_B + k_C[M])$$

for the rate of combination. The third-order rate constant is thus $k_A k_C/k_B$; the second-order rate constant is k_A; and the order of magnitude of the pressure at which the overall, termolecular, reaction changes from third to second order is given by

$$k_B = k_C[M]. \tag{12}$$

XY^* stands for a complex which possesses all the energy liberated by the association of the two particles X and Y. When X and Y are atoms, the resulting diatomic complex would be expected to have a lifetime of the same order of magnitude as the time for one vibration, i.e. $\sim 10^{-13}$ sec. Step (A) would be expected to occur on every collision of the two atoms, i.e. k_A should be $\sim 3 \times 10^{-10}$ (cm^3/atom) sec^{-1}. If, therefore, step (C) also occurs on every collision, i.e. if M is " perfectly efficient ", the rate constant for the third-order recombination of two atoms should be $\sim 10^{-32}$ (cm^3/atom)^2 sec^{-1}. It is well known that the combination of atoms in the presence of monatomic or most diatomic gases at ordinary pressures *is* in fact a third-order reaction with a rate constant around 10^{-32} (cm^3/atom)^2 sec^{-1}. It follows that, in the combination of atoms, (i) even very simple third bodies may be regarded as having approximately perfect efficiency,† (ii) the overall reaction would be expected to change order at a pressure very roughly equivalent to 3×10^{22} atom/cm^3, i.e. at a pressure around 2,000 atm at 200° C.

When XY^* is a polyatomic complex, its lifetime may be much greater than 10^{-13} sec because of the possibility of sharing the vibrational energy liberated by the association of X and Y over more than one mode of vibration. Many vibrations may have to occur before sufficient energy is present in the stretching mode of the X—Y bond for dissociation to take place. In such cases, provided that M is perfectly efficient, the third-order rate constant for the combination of

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† Where the efficiency appears abnormally great, it may be supposed that the reactions

$$X + M = XM^*$$

$$XM^* = X + M$$

$$XM^* + Y = XY + M$$

occur instead of (A), (B) and (C).

X and Y should be greater than 10^{-32} (cm^3/molecule)^2 sec^{-1}. Further, the greater the third-order rate constant, the lower should be the pressure around which the reaction changes from third to second order. Whereas one would expect all third bodies to have approximately the same efficiency for combination of two atoms via an energy-rich diatomic complex, a considerable specificity is to be expected in the efficiency of third bodies in radical combinations.[15]

Three independent lines of evidence, cited by Baldwin and Walsh,[16] lead to a value around 4×10^{-32} (cm^3/molecule)^2 sec^{-1} for the third-order rate constant at 520° C of the reaction

$$H + O_2 + H_2 = HO_2 + H_2. \tag{13}$$

From data of Robertson [17] it is possible to deduce [15] a value for the third-order rate constant of reaction (13) at 20° C equal to *ca.* 8×10^{-31} (cm^3/molecule)^2 sec^{-1}. From data of Patrick and Robb,[18] it is possible to deduce[15] a value for the rate constant at 20° C $\geqslant 5 \times 10^{-31}$ (cm^3/molecule)^2 sec^{-1}. These three values can be reconciled if one assumes a negative activation energy for reaction (13) equal to about 4 kcal/mole. There is independent evidence [15] to support a negative activation energy of about this magnitude. It would be caused by reaction (B) having a positive activation energy. We wish below to compare the rate constant of (13) with that for the third-order combination of methyl radicals. Data for the latter combination are only available for temperatures from 150 to 250° C. Assuming the third-order rate constant to vary as $T \exp (E/RT)$, where E is 4 kcal/mole and using the above data obtained at 20° C, a rate constant around 1×10^{-31} (cm^3/molecule)^2 sec^{-1} at 200° C is deduced.

There are reasons,[15] however, for believing that step (C) of reaction (13) does not occur on every collision. The most efficient third-body known for the general reaction

$$H + O_2 + M = HO_2 + M \tag{14}$$

is the water molecule. The rate constant of (14) is some ten times greater when M is H_2O than when M is H_2.[19] Using the value deduced above for reaction (13) at 200° C, one can conclude that at 200° C, when M is H_2O, reaction (14) would have a rate constant $\sim 10^{-30}$ (cm^3/molecule)^2 sec^{-1}. It becomes clear, in accord with the anticipation stated above, that, when M is perfectly efficient, the third-order rate constant for reaction (14) at all ordinary temperatures is appreciably greater than the rate constant for the combination of atoms (10^{-32} (cm^3/molecule)^2 sec^{-1}). Further, assuming as is plausible, that step (A) of reaction (14) occurs on every collision, one can calculate k_C/k_B and hence (by eqn. (12)) deduce that the reaction when M is H_2O, should change order in a pressure range around 20 atm at 200° C.

The data of Dodd and Steacie [6] lead to a value around 10^{-27} (cm^3/molecule)^2 sec^{-1} at temperatures from 150 to 250° C for the third-order rate constant of the reaction

$$CH_3 + CH_3 + M = C_2H_6 + M \tag{4'}$$

when acetone is the third body. The probability is that acetone is an almost perfectly efficient third body.[15] (Only acetaldehyde is known [6] to exceed acetone in efficiency as a third body and then only by a factor of 3.) For reasons given above, it was to be expected that the maximum third-order rate constant for (4′) would be considerably greater than *ca.* 10^{-32} (cm^3/molecule)^2 sec^{-1}. It is known [6, 20] that the steric factor for reaction (4) when second order is not far from unity. It follows that step (A) of reaction (4′) when third order has almost the same rate as the conventionally calculated collision frequency for two methyl radicals. It further follows, from eqn. (12), that the order of reaction (4′), when M is acetone, should change in a pressure range roughly around 10 mm of acetone at 200° C. This conclusion agrees reasonably well with the experimental data.[6, 20]

Now the lifetime of XY* should be greater the greater the sharing of the vibrational energy of XY* over its various vibrational degrees of freedom. Provided the steric factor of step (A) is kept constant and provided we are referring to a third body of maximum efficiency, the overall third-order rate of combination of X and Y should also be greater the greater the sharing of the vibrational energy of XY* over its various vibrations, The extent of this sharing will depend upon several factors. Two of the most important will be (i) the complexity of XY, (ii) the vibrational energy possessed by XY*. As regards (i) the more vibrations there are over which to share the energy of XY*, the greater will tend to be the lifetime of XY*. As regards (ii), the greater the total energy (which can be imagined as initially all in the stretching vibration of the X—Y bond) the greater will be the chance of it approximating to some combination of other fundamental vibration frequencies or their overtones; this, by Fermi resonance, would lead to a distribution of the total energy over many vibrational modes. As regards comparison of reactions (14) and (4′), the C_2H_6 molecule has so many more vibrational modes than the HO_2 radical, and the exothermicity of (4′) is so much greater than that of (14), that it is in no way surprising that the maximum rate constant for (4′) should be not merely—as deduced above—considerably greater than the rate constant for atomic combinations, but also considerably greater than the maximum rate constant of (14). The CH_3OO radical has a complexity intermediate between that of the C_2H_6 molecule and that of the HO_2 radical, but (3′) is expected to be considerably less exothermic than either (14) or (4′). As regards comparison of reactions (3′) and (4′), therefore, factors (i) and (ii) above reinforce each other and it seems highly probable that the maximum rate constant of (3′) though greater than the rate constant for atomic recombinations, should be much less than the maximum rate constant of (4′). As regards comparison of reactions (3′) and (14), factors (i) and (ii) oppose each other. Therefore the rate constants of reactions (3′) and (14) could be similar in magnitude. As with reaction (4′) acetone is likely to be an almost perfectly efficient third body for reaction (3′). The expectation that the maximum rate constant of (3′) should lie in the range 10^{-32} to 10^{-27} $(cm^3/molecule)^2$ sec^{-1} therefore carries with it the expectation that (3′) should be third order below a pressure of acetone lying between ~ 10 mm and ~ 2,000 atm at 200° C. More particularly, what we have said above about the lifetime of CH_3OO^* makes the expectation that reaction (3′) should be third order below, say, 200 mm of acetone a rather strong one.

The conclusions from our experimental work, viz. that reaction (3′) at 200° C is third order at pressures up to at least 200 mm of acetone and has a third-order rate constant of $1{\cdot}6 \times 10^{-31}$ $(cm^3/molecule)^2$ sec^{-1} when M is acetone, are in accord with the above theoretical expectations.

THE REACTION $CH_3 + NO + M = CH_3NO + M$

The association of CH_3 radicals and NO molecules to give nitrosomethane molecules has commonly been assumed to be a second-order reaction. With such an assumption, Durham and Steacie[21] found the rate constant of the reaction to be $5{\cdot}5 \times 10^{-14}$ $(cm^3/molecule)^2$ sec^{-1} at 200° C. This estimate was obtained from a study of the pyrolysis of 0·2 mm di-*tert.*-butyl peroxide in the presence of much smaller quantities of nitric oxide. Assuming zero activation energy and a collision number of $3{\cdot}7 \times 10^{-10}$ $(cm^3/molecule)^2$ sec^{-1}, the estimate implies a steric factor of $1{\cdot}5 \times 10^{-4}$. As discussed above for the association of CH_3 radicals with O_2 molecules, this steric factor is surprisingly low in view of the known steric factor for the association of two CH_3 radicals. The slowness of the reaction can be explained in another way, viz. by supposing the reaction to be third order at the pressures used. In view of the fact that even the reaction of two CH_3 radicals to give ethane would not be second order at the very low pressures used in the work of Durham and Steacie, such a supposition is almost certainly correct. The third-order rate constant at 200° C and when M is di-*tert*.-butyl peroxide works out to be $9{\cdot}0 \times 10^{-30}$ (cm^3/molecule)^2 sec^{-1}.

Even at much higher pressures, the theoretical expectations given above and comparison with reaction (3′) would strongly suggest the expectation that CH_3 radicals and NO molecules associate in a third-order reaction. At 480° C and in the presence of a large excess of helium (10 mm) Bryce and Ingold[22] find the rate constant for a supposed second-order reaction of CH_3 radicals and NO molecules to be $2{\cdot}2 \times 10^{-13}$ (cm^3/molecule) sec^{-1}. If the reaction is taken to be third order, the third-order rate constant, at 480° C and when M is helium works out to be $1{\cdot}7 \times 10^{-30}$ (cm^3/molecule)^2 sec^{-1}. From similar data of Bryce and Ingold, a third-order rate constant, at 900° C and when M is helium, may be calculated to be $2{\cdot}8 \times 10^{-30}$ (cm^3/molecule)^2 sec^{-1}.

Chilton and Gowenlock[23] find the rate constant for an assumed second-order association of an *iso*propyl radical and an NO molecule to be less than or equal to one-tenth of the rate constant for the second-order association of two *iso*propyl radicals. If both reactions *were* second order under the conditions used it would be difficult to understand the relative slowness of the reaction with nitric oxide. It is quite likely, however, that at the extremely low pressures used (approx. 4 mm) the association with nitric oxide was tending towards third order, while the association of the two *iso*propyl radicals was still second order.

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