815. *Reactions of the Isopropoxyl Radical. Part I. Pyrolysis of Isopropyl Nitrite in a Static System at* 175—200°

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The kinetics of the various possible reactions postulated for the pyrolysis of alkyl nitrites have been considered in reference to isopropyl nitrite at 175—200°/35 mm. The mechanism involving intermediate formation of nitroxyl, suggested by Levy, is confirmed, but abstraction of nitric oxide from the nitrite by methyl radicals produced by pyrolysis of isopropoxyl also occurs; direct disproportionation of isopropoxyl does not occur. The rate constant for decomposition of isopropoxyl is

$$k_4 \sim 4 \cdot 5 \times 10^{10} \exp(-16{,}000/\boldsymbol{R}T) \text{ sec.}^{-1}$$

on the assumption of first-order kinetics. The decrease in the rate of pyrolysis of the nitrite observed at 190—200°, with and without initially added nitric oxide, is explained on the basis of the various reactions competing for isopropoxyl. In the presence of added nitric oxide, the rate constant k_{12} for production of nitrous oxide by bimolecular decomposition of nitroxyl is 10^9—10^{11} mole^{-1} cm.^{3} sec.$^{-1}$ at 190°.

Much information now exists on the pyrolysis of methyl,[1] ethyl,[2] and a series of more complex mononitrites,[3] and the general reaction scheme is fairly well established. Little quantitative data is available for isopropyl nitrite, which is of particular interest in that it

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[1] P. Gray and A. Williams, *Nature*, 1960, **188**, 56; L. Phillips, *J.*, 1961, 3082.

[2] J. B. Levy, *J. Amer. Chem. Soc.*, 1953, **75**, 1801.

[3] P. Gray, P. Rathbone, and A. Williams, *J.*, 1960, 3932; 1961, 2620; P. Gray, M. J. Pearson, and P. Rathbone, *J.*, 1961, 4006.

should provide a convenient source for studying the decomposition of the isopropoxyl radical.

The pyrolysis of isopropyl nitrite was first studied by Steacie and Shaw,[4] who made use of pressure measurements. Analysis of their products was very inadequate, judged by modern standards, and, although some of the features of the suggested mechanism are correct, the detail is not consistent with present theory. Levy [5] carried out a qualitative investigation based on product identification by infrared spectroscopy, and suggested a mechanism similar to that for ethyl nitrite;[2] an additional step, involving decomposition of the isopropoxyl radical into acetaldehyde and a methyl radical, was invoked.

The present Paper presents a quantitative mechanistic investigation of the pyrolysis of isopropyl nitrite in a static system at 175—200°, with particular reference to the reactions of the isopropoxyl radical and of nitroxyl.

EXPERIMENTAL

Materials.—Isopropyl nitrite was prepared from isopropyl alcohol and nitrous acid. Concentrated sulphuric acid (73·5 g.), water (30 ml.), and 97% of propan-2-ol (90 g.) were cooled to 0° and added to sodium nitrite (113·8 g.), in water (500 ml.) at −5° during 1 hr., the temperature being kept at about 0°. The isopropyl nitrite was separated, dried (Na_2SO_4), and fractionated twice *in vacuo*, the middle cut being retained and stored at −40° *in vacuo* in the dark.

Nitric oxide was prepared by heating a mixture of potassium nitrite, potassium nitrate, chromic oxide, and ferric oxide.[6] It was fractionated between liquid oxygen and nitrogen traps, and mass-spectrometric analysis then showed it to be 99·9% pure.

Procedure.—Pyrolysis was carried out in a conventional static type of apparatus, with a 150-ml. Pyrex reactor fitted with a Pyrex spiral glass manometer, which was electrically heated to prevent condensation. The electrically heated furnace was kept to within ±0·1° of the required temperature by a Sunvic RT2 controller. The initial reactant pressure was 35 mm. After predetermined times, the products were expanded into an infrared cell with sodium chloride windows, *via* electrically heated connecting tubing. The wavelengths used for infrared analysis were, isopropyl nitrite 6·04, 12·85, acetaldehyde 3·68, acetone 5·74, formaldoxime 11·44, 10·52, propan-2-ol 10·52, nitrous oxide 4·5 μ, allowance being made where necessary for overlapping absorptions. The products were pressurised to 400 mm. with nitrogen to allow for possible pressure-broadening effects. As the estimation of nitric oxide at 5·25 μ was not accurate enough for our purpose, the determination was made by mass-spectrometry in some cases, after the products had been fractionated in a Leroy still at −193 and −150°.

RESULTS

Results of typical product analyses at 200, 190, and 175° are given in Table 1. Carbon balances usually range from 0·92 to 1·05; some losses of formaldoxime occur, probably because of polymerisation in the cold infrared cell. The yields of nitric oxide, on the basis of Levy's [5] suggested mechanism, should equal acetone plus propan-2-ol; this has been confirmed by fractionation and mass-spectrometric estimation as previously mentioned. Thus, after 25 min. at 200°, 0·36 moles of nitric oxide were obtained as compared with $[Me_2CO] + [IPA] = 0{\cdot}34$. Nitrogen (possibly with some carbon monoxide), 0·008 mole, and methane, 0·001 mole, were also found.

The effects on product distribution, after 45 min. at 190°, of adding varying amounts of nitric oxide are shown in Table 2, and of the variations with time produced by adding a constant amount of nitric oxide in Table 3.

Yields of acetone are increased at the expense of acetaldehyde, and nitrous oxide is formed in increasing amounts as nitric oxide increases, at the expense of propan-2-ol, which is in agreement with Levy's [5] qualitative observations. The rate of decomposition of the nitrite is also reduced.

[4] E. W. R. Steacie and R. Shaw, *Proc. Roy. Soc.*, 1935, *A*, **151**, 685.

[5] J. B. Levy, *Ind. Eng. Chem.*, 1956, **48**, 762.

[6] J. D. Ray and R. A. Ogg, *J. Amer. Chem. Soc.*, 1956, **78**, 5993.

TABLE 1

Products (moles/mole of initial nitrite) of reactions at various temperature

Time (min.)	MeCHO	Me_2CO	Me_2·CH·ONO [IPN]	Me_2·CH·OH [IPA]	CH_2:NOH
At 200°					
5	0·117	0·061	0·760	0·087	0·078
10	0·157	0·100	0·608	0·109	0·100
15	0·195	0·135	0·506	0·130	0·113
25	0·223	0·175	0·354	0·166	0·131
35	0·238	0·209	0·241	0·209	0·134
60	0·282	0·296	0·110	0·320	0·166
At 190°					
15	0·109	0·075	0·730	0·087	0·087
30	0·130	0·142	0·606	0·130	0·099
47	0·164	0·189	0·426	0·192	0·104
60	0·180	0·218	0·357	0·218	0·109
90	0·206	0·277	0·255	0·266	0·106
At 175°					
30	0·047	0·053	0·888	0·088	0·024
60	0·079	0·082	0·776	0·106	0·035
120	0·123	0·168	0·594	0·190	0·039
180	0·147	0·192	0·483	0·218	0·062
240	0·152	0·231	0·386	0·260	0·059

Nitric oxide was present throughout, but results by infrared estimation were not accurate enough. Traces of hydrogen cyanide and nitrous oxide were also formed.

TABLE 2

Effect of added nitric oxide on reaction at 190° for 45 min.

	Added NO		
Product	0	0·2	1·0
MeCHO	0·17	0·067	0·020
Me_2CO	0·180	0·217	0·242
Me_2·CH·ONO	0·440	0·576	0·729
Me_2·CH·OH	0·183	0·154	0·085
CH_2:NOH	0·104	0·019	0
N_2O	0·007	0·022	0·088

TABLE 3

Effect of addition of 0·62 mole NO/mole of initial Pr^iONO

	Time (min.)			
Product	30	45	60	90
MeCHO	0·018	0·029	0·044	0·060
Me_2CO	0·164	0·230	0·285	0·379
Me_2·CHONO	0·766	0·608	0·579	0·405
Me_2·CHOH	0·043	0·056	0·067	0·090
CH_2:NOH	0·014	0·033	0·038	0·048
N_2O	0·057	0·074	0·089	0·098

Addition of acetaldehyde in an amount roughly equal to that formed on complete decomposition of the nitrite resulted in a 20% increase in propan-2-ol after 45 min. at 190°, indicating attack by the isopropoxyl radical on the acetaldehyde (reaction 7).

Increasing the surface: volume ratio of the reactor by a factor of about ten, by packing it with Pyrex tubing had no effect on product-distribution or rate of decomposition.

DISCUSSION

Stoicheiometry and Reaction Mechanism.—Product analyses confirm the mechanism suggested by Levy [5]

$$Me_2\cdot CH\cdot O\cdot NO \rightleftharpoons Me_2\cdot CHO\cdot + NO \tag{1}$$

$$Me_2\cdot CHO\cdot + NO \longrightarrow Me_2\cdot CO + HNO \tag{2}$$

$$Me_2\cdot CHO\cdot + HNO \longrightarrow Me_2\cdot CHOH + NO \tag{3}$$

$$Me_2\cdot CHO\cdot \longrightarrow Me\cdot + Me\cdot CHO \tag{4}$$

$$Me\cdot + NO + M \longrightarrow MeNO + M \tag{5}$$

$$MeNO \longrightarrow CH_2\!:\!NOH \tag{6}$$

As the carbon balances are good, no major product is left undetected. Stoicheiometry demands that the yields of acetone and propan-2-ol should be equal, and this is true at 200 and 190°. The yields of nitric oxide at 200° are equal to acetone plus propan-2-ol, as required by the mechanism. Acetaldehyde exceeds formaldoxime, probably because of losses of the latter through polymerisation during estimation; the yields of nitrogen at 200 are negligible so that, under our conditions, further reactions between nitrosomethane and nitric oxide [7] are insignificant, although Levy [5] reports the formation of small amounts of nitromethane, which is a product of such reactions.[8]

The equality of the yields of acetone and propan-2-ol at 200 and 190° might be explained on the basis of disproportionation of isopropoxyl

$$2Me_2{\cdot}CHO{\cdot} \longrightarrow Me_2{\cdot}CHOH + Me_2CO \qquad (7)$$

as suggested by Phillips [1] for the methoxyl radical. However, calculation of the rate of recombination of isopropoxyl

$$2Me_2{\cdot}CHO{\cdot} \longrightarrow Me_2CH{\cdot}O{\cdot}O{\cdot}HCMe_2 \qquad (8)$$

from the relationship

$$R \ln A_8/A_{-8} = \Delta S + R + 20{\cdot}1$$

assuming A_{-8} to be the same as for other organic peroxides, *i.e.*, 10^{14} mole^{-1} cm.^{3} sec.$^{-1}$ according to Hanst and Calvert,[9] and entropies of 71·5 and 105·9 e.u., calculated for isopropoxyl and di-isopropyl peroxide from the additivity rules of Benson and Buss,[10] gives $A_8 = 4 \times 10^{10}$ mole^{-1} cm.^{3} sec.$^{-1}$. Since $E_8 = 0$, $A_8 = k_8$. Disproportionation: combination ratios for alkoxyl radicals are very high,[11] so k_7 is not less than 10^{11}—10^{12} mole^{-1} cm.^{3} sec.$^{-1}$. Arden and Phillips,[12] using MacMillan's results [13] for k_2/k_{-1} determined from reaction of isopropyl (derived from the peroxide) with nitric oxide, and a value of $k_{-1} = 6{\cdot}3 \times 10^{10}$ mole^{-1} cm.^{3} sec.$^{-1}$ calculated from the above entropy relationship, found $k_2 \simeq 10^{10}$ mole^{-1} cm.^{3} sec.$^{-1}$. Since

$$R(Me_2CO)\ (\text{reaction } 2)/R(Me_2CO)\ (\text{reaction } 7) = k_2[NO]/k_7[Me_2{\cdot}CHO{\cdot}],$$

reaction (7) cannot compete with reaction (2), except possibly in the very early stages ($\ll 1\%$) of decomposition, when nitric oxide pressures are very low. Similar arguments can be advanced against disproportionation of methoxyl radicals in methyl nitrite pyrolysis.

The possible reaction

$$Me_2{\cdot}CHO{\cdot} + Me_2{\cdot}CH{\cdot}O{\cdot}NO \longrightarrow Me_2{\cdot}CHOH + Me_2{\cdot}CO + NO \qquad (9)$$

is unlikely to compete for isopropoxyl, because yields of carbon monoxide at 200° indicate that the attack on acetaldehyde by isopropoxyl

$$Me_2{\cdot}CHO{\cdot} + MeCHO \longrightarrow Me_2{\cdot}CHOH + MeCO{\cdot} \qquad (10)$$

is negligible. (Hoare [14] has shown that the acetyl radical readily decomposes to carbon monoxide in the presence of nitric oxide at 200°.) Methyl radicals abstract hydrogen from acetaldehyde about ten times faster than from propan-2-ol [15] at 200°, and at about the same rate from propan-2-ol and isopropyl nitrite.[16] On the reasonable assumption that the ratio of the rates of hydrogen abstraction from acetaldehyde and isopropyl nitrite is about the same for isopropoxyl and methyl, it is clear that reaction (9) must be negligible.

The observation that, at 175°, the amount of propan-2-ol exceeds that of acetone must indicate the occurrence of another abstraction reaction of the isopropoxyl radical, which

[7] O. P. Strausz and H. E. Gunning, *Canad. J. Chem.*, 1963, **41**, 1207; E. A. Arden and L. Phillips, *J.*, 1964, 5118.

[8] L. Phillips and R. Shaw, Xth International Symposium on Combustion, Discussion on Elementary Reactions, Cambridge, August 1964.

[9] P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, 1959, **63**, 104.

[10] S. W. Benson and J. H. Buss, *J. Chem. Phys.*, 1958, **29**, 546.

[11] M. H. J. Wijnen, *J. Amer. Chem. Soc.*, 1958, **80**, 2394; D. F. Dever and J. G. Calvert, *ibid.*, 1962, **84**, 1362.

[12] E. A. Arden, L. Phillips, and R. Shaw, *J.*, 1964, 5126.

[13] G. R. McMillan, *J. Amer. Chem. Soc.*, 1961, **83**, 3018.

[14] D. E. Hoare, *Canad. J. Chem.*, 1962, **40**, 2012.

[15] A. F. Trotman-Dickenson, " Gas Kinetics," Butterworth, London, 1955, p. 201.

[16] J. M. Ferguson and L. Phillips, unpublished work.

does not produce acetone. Reaction (10) is negligible at 200° and, since $E_{10} > E_2$, should not compete at 175°. A possibility is

$$\mathrm{Me_2{\cdot}CHO{\cdot} + CH_3{\cdot}NO \longrightarrow Me_2{\cdot}CHOH + {\cdot}CH_2{\cdot}NO} \qquad (11)$$

which has been postulated by Bromberger and Phillips;[17] since E_6 is about [18] 35 kcal.mole^{-1}, reaction (11) should be favoured by lower temperatures.

The effects of initially added nitric oxide (Tables 2 and 3) are in agreement with the suggested mechanism. Thus, yields of acetone increase at the expense of acetaldehyde, formaldoxime is reduced, and nitrous oxide is formed in amounts increasing with nitric oxide pressure, indicating that the increased rate of production of nitroxyl allows reaction (12) to become important at the expense of reaction (3)

$$\mathrm{2HNO \longrightarrow H_2O + N_2O} \qquad (12)$$

Table 5 shows that the relationship $[\mathrm{Me_2{\cdot}CO}] - [\mathrm{Me_2{\cdot}CHOH}] = 2[\mathrm{N_2O}]$ holds in the early stages at 190°, but that the right-hand side becomes progressively less than the left-hand side as reaction proceeds. This may be due to reaction of nitroxyl with nitric oxide as suggested by Arden and Phillips [19] and by Strausz and Gunning [7]

$$\mathrm{HNO + 2NO \longrightarrow HN(NO)O{\cdot}NO} \qquad (13)$$

$$\mathrm{HN(NO)O{\cdot}NO \longrightarrow H{\cdot} + N_2 + {\cdot}NO_3} \qquad (14)$$

$$\mathrm{{\cdot}NO_3 + NO \longrightarrow 2NO_2} \qquad (15)$$

Steacie and Shaw [4] found that the overall first-order rate-constant, *k*, for the decomposition of isopropyl nitrite, determined from pressure/time curves, decreases as the reaction proceeds. Our results based on nitrite estimation (Table 4), show a progressive but decreasing fall in *k* at 190 and 200° as the reaction proceeds; similar effects were observed when nitric oxide was added initially (Table 4). Levy [5] reported a similar, but greater, effect of added nitric oxide on the rate of pyrolysis of t-butyl nitrite, and suggested that it was due to enhancement of the rate of recombination of the t-butoxyl radical with nitric oxide. Whilst such an explanation may appear plausible for isopropyl nitrite with and without added nitric oxide, it has difficulties, in that it is not observed with methyl and ethyl nitrites. Gray [20] has pointed out that the retardation with t-butyl nitrite must be due, at least in part, to suppression of the abstraction of nitric oxide from the nitrite by methyl radicals, which are preferentially removed by reaction (5). Bromberger and Phillips [17] have demonstrated the occurrence of this reaction with isopropyl nitrite and methyl radicals,

TABLE 4

Variation of *k* with extent of reaction

200°		190°		175°	
Reaction (%)	10^3k (min.$^{-1}$	Reaction (%)	10^3k (min.$^{-1}$)	Reaction (%)	10^3k (min.$^{-1}$)
24·0	55	18·5	20·7	11·2	3·94
39·2	50	31·5	18·9	22·4	4·25
49·4	46	42·0	18·1	32·0	4·28
58·0	43	51·5	18·1	40·0	4·28
64·6	42	58·5	17·6	46·0	4·10
70·7	41	64·0	17·1	51·7	4·04
75·9	41	68·0	16·6	58·3	4·16
80·0	40	72·0	15·9		

$$\mathrm{Me{\cdot} + Me_2{\cdot}CH{\cdot}O{\cdot}NO \longrightarrow MeNO + Me_2CHO{\cdot}} \qquad (16)$$

and its occurrence here is strongly suggested by the fact that little or no retardation occurs at 175°, where the formation of methyl radicals by the decomposition of isopropoxyl

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[17] B. Bromberger and L. Phillips, *J.*, 1961, 5302.

[18] B. G. Gowenlock and W. Lüttke, *Quart. Rev.*, 1958, **12**, 321.

[19] E. A. Arden and L. Phillips, *Proc. Chem. Soc.*, 1962, 354, and ref. 7.

[20] P. Gray, *Chem. and Ind.*, 1960, 120.

(reaction 4) is much less than at 190 and 200°. The reduction in acetaldehyde and increase in acetone caused by the addition of nitric oxide (Table 2) shows that the decreases observed in k are due mainly to preferential removal of isopropoxyl by reaction with nitric oxide (reaction 2) and the consequent suppression of reaction (16). This is not the case with t-butyl nitrite where reaction (2) cannot occur; retardation in this case is due to the removal of methyl by reaction (5).

Heterogeneous reactions appear to be unimportant (which is in agreement with Steacie and Shaw [4]) since increase in surface : volume ratio of the reactor had no effect on the products or their distribution.

Kinetics of Decomposition of the Isopropoxyl Radical.—On the basis of the above mechanism, the only reactions producing acetone and acetaldehyde are

$$\mathrm{Me_2{\cdot}CHO{\cdot} + NO \longrightarrow HNO + Me_2{\cdot}CO} \qquad (2)$$

and

$$\mathrm{Me_2{\cdot}CHO{\cdot} \longrightarrow Me{\cdot} + Me{\cdot}CHO} \qquad (4)$$

so that

$$R(\mathrm{Me_2{\cdot}CO})/R(\mathrm{Me{\cdot}CHO}) = k_2[\mathrm{NO}]/k_4$$

Taking $[\mathrm{NO}] = [\mathrm{Me_2{\cdot}CO}] + [\mathrm{Me_2{\cdot}CHOH}] = 2[\mathrm{Me_2{\cdot}CO}]$, which holds at 190 and 200°, and probably at 175° if allowance is made for extra propan-2-ol produced by reaction (11), and $R(\mathrm{Me_2{\cdot}CO})$ and $R(\mathrm{Me{\cdot}CHO})$ determined from the slopes of the product/time curves at times corresponding to about 7% decomposition, gives the following results:

	200°	190°	175°
$R(\mathrm{Me{\cdot}CHO})$ (mm. sec.$^{-1}$)	$2{\cdot}45 \times 10^{-2}$	$5{\cdot}95 \times 10^{-3}$	$1{\cdot}05 \times 10^{-3}$
$R(\mathrm{Me_2{\cdot}CO})$ (mm. sec.$^{-1}$)	$8{\cdot}75 \times 10^{-3}$	$3{\cdot}85 \times 10^{-3}$	$1{\cdot}05 \times 10^{-3}$
[NO] (mm.)	1·96	2·02	1·96
k_2/k_4 (mole^{-1} cm.^{3})	$5{\cdot}37 \times 10^6$	$9{\cdot}25 \times 10^6$	$14{\cdot}23 \times 10^6$

A plot of log k_2/k_4 against $1/T$ gives $E_2 - E_4 \sim -16$ kcal. mole^{-1}. McMillan's results [13] for k_2/k_{-1} show that E_2 is approximately zero, and Arden, Phillips, and Shaw [12] find that the corresponding reaction between ethoxyl radicals and nitric oxide has zero activation energy; hence $E_4 \sim 16$ kcal. mole^{-1}. Wijnen,[21] in studies on the photolysis of isopropyl propionate found $E_4 - E_{17} < 6$ kcal.mole^{-1}

$$\mathrm{Me_2CHO{\cdot} + Me_2CHOOCEt \longrightarrow Me_2CHOH + Me_2\dot{C}OOC{\cdot}Et} \qquad (17)$$

assuming that the tertiary hydrogen atom was abstracted from the propionate. Assuming E_{17} is the same as for methoxyl attack on isobutane,[22] *i.e.*, 4·2 kcal.mole^{-1}, this gives $E_4 < 10{\cdot}2$ kcal.mole^{-1}. Wijnen, however, invoked the presence of " hot " isoproproxyl radicals in the treatment of his results, and his value of $E_4 - E_{17}$ may be open to doubt. The present results, however, are only approximate, because of difficulties in assessing the slopes of product/time curves based on infrared measurements. The enthalpy change [23] of about 7 kcal.mole is not inconsistent with either of the above results.

The only other alkoxyl radicals for which activation energies for C–C bond fission have been reported are t-butoxyl and ethoxyl. Gray and Williams,[23] from a review of existing data, suggest a value of 13 ± 2 kcal.mole^{-1} for t-butoxyl, which is considered less stable than isopropoxyl, whilst more recent work by McMillan [24] gives 11 ± 2 kcal.mole^{-1}. For ethoxyl, values of 28—34 kcal.mole^{-1} based on the photolysis of diethyl ether,[23] and 21 kcal.mole^{-1} based on the photolysis of ethyl nitrite [24] are suggested, whilst Wijnen [21] reports a value of ~13 kcal.mole^{-1}. The latter result is likely to be low, because the necessary enthalpy change is 13 kcal.mole^{-1}. For elimination of methyl from the isobutyl

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[21] M. H. J. Wijnen, *J. Amer. Chem. Soc.*, 1960, **82**, 3034.

[22] T. Bercés and A. F. Trotman-Dickenson, *J.*, 1961, 348.

[23] P. Gray and A. Williams, *Chem. Rev.*, 1959, **59**, 239.

[24] G. R. McMillan, *J. Amer. Chem. Soc.*, 1960, **82**, 2422.

radical, which is isoelectronic with isopropoxyl, Kerr and Trotman-Dickenson [25] quote a value of 26 kcal.mole^{-1}, which they consider is low.

Using the value of $k_2 = 10^{10}$ mole^{-1} cm.^{3} sec.$^{-1}$ calculated by Arden, Phillips, and Shaw,[12] and the present value of $k_2/k_4 = 5{\cdot}4 \times 10^6$ mole^{-1} cm.^{3}, we find $k_4 = 1{\cdot}8 \times 10^3$ sec.$^{-1}$ at 200°. Taking $E_4 = 16$ kcal.mole^{-1}, this gives $A_4 = 4{\cdot}5 \times 10^{10}$ sec.$^{-1}$. Similar low values of the frequency factor for the pyrolysis of t-butoxyl have been reviewed by Hershenson and Benson,[26] who consider that they imply pressure-dependence, for which they have direct evidence. This possibility for the decomposition of isopropoxyl is being examined and will be the subject of a later Paper. If reaction (4) is pressure-dependent

$$\mathrm{Me_2{\cdot}CHO{\cdot} + M \longrightarrow Me{\cdot} + Me{\cdot}CHO + M} \qquad (4,\ M)$$

$k_{4\mathrm{M}} = k_4/[\mathrm{M}]$, which with $[\mathrm{M}] = 9{\cdot}4 \times 10^{-7}$ mole cm.$^{-3}$ becomes 2×10^9 mole^{-1} cm.^{3} sec.$^{-1}$, and with $E_{4\mathrm{M}} \simeq 16$ kcal.mole^{-1}, $A_{4\mathrm{M}} \sim 4{\cdot}9 \times 10^{16}$ mole^{-1} cm.^{3} sec.$^{-1}$.

The Rate of Decomposition of Nitroxyl.—Results obtained on the effect of added nitric oxide (0·61 mole/mole isopropyl nitrite) at 190°, gave the following initial rates of product formation,

	Moles/mole nitrite used		Moles/mole nitrite used		Moles/mole nitrite used
R(Me·CHO)...	$1{\cdot}2 \times 10^{-5}$	R(Me$_2$·CHOH)	$2{\cdot}8 \times 10^{-5}$	R(N$_2$O)	$3{\cdot}3 \times 10^{-5}$

which enable an approximate value of k_{12} to be determined. From reactions (3), (4), and (12), it can be shown, when reaction (11) is negligible, as is the case in the very early stages of decomposition, that $R(\mathrm{Me_2{\cdot}CHOH})/\mathrm{R}(\mathrm{Me{\cdot}CHO}) = k_3[\mathrm{HNO}]/k_4$, and since $[\mathrm{HNO}] = [R(\mathrm{N_2O})]^{\frac{1}{2}}/k_{12}^{\frac{1}{2}}$, $R(\mathrm{Me_2{\cdot}CHOH})/R\mathrm{Me{\cdot}CHO}) = k_3[R(\mathrm{N_2O})]^{\frac{1}{2}}/k_4k_{12}^{\frac{1}{2}}$. Converting $R_{(\mathrm{N_2O})}$ to mole cm.$^{-3}$ sec.$^{-1}$ units gives $[R(\mathrm{N_2O})]^{\frac{1}{2}} = 6{\cdot}3 \times 10^{-6}$ mole$^{\frac{1}{2}}$ cm$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$. Taking the present value of $k_2/k_4 = 9{\cdot}3 \times 10^6$ mole^{-1} cm.^{3}, and $k_2 = 10^{10}$ mole^{-1} cm.^{3} sec.$^{-1}$ as before, gives $k_4 \simeq 10^3$ sec.$^{-1}$ at 190°, whence $k_3/k_{12}^{\frac{1}{2}} = 3{\cdot}6 \times 10^8$ mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$. The value of k_3 is not known but since, when no nitric oxide is initially added, nitrous oxide formation is negligible, a steady-state treatment for nitroxyl gives

$$k_2[\mathrm{Me_2{\cdot}CHO{\cdot}}][\mathrm{NO}] = k_3[\mathrm{Me_2{\cdot}CHO{\cdot}}][\mathrm{HNO}]$$

so that, because $[\mathrm{NO}] \gg [\mathrm{HNO}]$, $k_3 \gg 10^{10}$ mole^{-1} cm.^{3} sec.$^{-1}$. Taking various possible values for k_3 gives the following for k_{12}

k_3 (mole^{-1} cm.^{3} sec.$^{-1}$)	k_{12} (mole^{-1} cm.^{3} sec.$^{-1}$)
10^{12}	9×10^6
10^{13}	9×10^8
10^{14}	9×10^{10}

These values should be compared with $k_{12} > 3 \times 10^7$ mole^{-1} cm.^{3} sec.$^{-1}$ found by Clyne [27] from the reaction of nitric oxide with hydrogen atoms at ambient temperature. It is unlikely that k_3 will be as high as 10^{14} mole^{-1} cm.^{3} sec.$^{-1}$; 9×10^8 mole^{-1} cm.^{3} sec.$^{-1}$ may well be a realistic value for k_{12}.

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[25] J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Reaction Kinetics," ed. G. Porter, Pergamon, London, 1961, vol. I, p. 123.

[26] H. Hershenson and S. W. Benson, *J. Chem. Phys.*, 1962, **37**, 1889.

[27] M. A. Clyne, Xth International Symposium on Combustion, Cambridge, August 1964.