190. *Homolytic Substitution at a Saturated Carbon Atom. Part III.*[1] *Kinetics of the Gaseous Reaction of Nitric Acid in Nitrogen alone and in the Presence of Methane.*

By Tessa S. Godfrey, (the late) E. D. Hughes, and Sir Christopher Ingold.

The gaseous self-decomposition of nitric acid, 10—48 mm., made up with nitrogen to 680 mm., has been followed at 303·5 and 349·5° by means of the pressure change. The same reaction has been studied by means of infrared analysis at 349·5°, more definitively, and as the reference-reaction for a corresponding study of the reaction between nitric acid, 5—17 mm., and methane, 90—700 mm., with nitrogen added as needed to make up a minimum total pressure of 700 mm.

Confirming the conclusions of Johnston and his co-workers, we find the self-decomposition of nitric acid to have the kinetics of a unimolecular reaction, in which the rate-controlling first step of homolysis is reversible. We find the reaction with methane to have the kinetics, apart from a small rate-dependence on methane, of a unimolecular reaction rate-controlled by the same first step of homolysis, which is here irreversible, because it is followed by fast reactions, as shown in eqns. (12) (p. 1077). These reactions lead in parallel to nitration and oxidation, at absolute rates, and with product compositions, which are plausibly consistent with observation. The small dependence of the rate on methane concentration may be the superposed effect of a concurrent, relatively unimportant, bimolecular heterolytic mechanism, as illustrated in eqn. (13) (p. 1077).

The work of Part I [2] was designed to show whether the gaseous nitration of alkanes is a process dependent on radicals. If alkyl radicals were intermediately formed, the gaseous nitration of t-butylbenzene would produce the neophyl radical, $PhCMe_2{\cdot}CH_2{\cdot}$, which would disclose itself by rearrangement. It was shown that the gaseous nitration of t-butylbenzene occurs only in the t-butyl group, and that products of rearrangement of the neophyl radical are formed. As a check on the method, gaseous photochemical chlorination, which is known to be a radical-dependent reaction, was examined similarly, as described in Part II.[1] t-Butylbenzene was thus chlorinated exclusively in the t-butyl group, and the expected rearrangement occurred.

We now pass from these studies of products to the kinetics of gaseous nitration. A homolytic mechanism involving alkyl radicals would have to depend on radicals which had been previously formed by homolysis of the nitrating agent, in our work, nitric acid. We therefore began with a kinetic study of the gaseous decomposition of nitric acid in the absence of an alkane. This is a subject on which there has been important previous work.

(1) *The Gaseous Decomposition of Nitric Acid.*—(1.1) *Previous work.* Fréjaques [3] studied this decomposition at somewhat low vapour pressures in the absence of a gaseous diluent at 280—475°. He followed the formation of nitrogen dioxide photometrically, or, under some conditions, followed the change of pressure, deducing the progress of destruction of nitric acid from either form of measurement, by assuming the stoicheiometry of eqn. (1):

$$2HNO_3 = 2NO_2 + H_2O + \tfrac{1}{2}O_2 \qquad (1)$$

He found the reaction to be substantially homogeneous above 300°. His initial rate varied as the square of the concentration of nitric acid, and his continuing reactions had a complicated form. He proposed the bimolecular mechanism (2), rate-controlled by the

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[1] Part II, Backhurst, Hughes, and Ingold, *J.*, 1959, 2742.
[2] Part I, Duffin, Hughes, and Ingold, *J.*, 1959, 2734.
[3] Fréjaques, *Mem. Poudres*, 1953, **35**, appendix.

self-dehydration of nitric acid, the formed dinitrogen pentoxide then decomposing rapidly in the manner already elucidated by Ogg.[4]

$$\left.\begin{array}{r}2HNO_3 \longrightarrow H_2O + N_2O_5\\ N_2O_5 \rightleftharpoons NO_2 + NO_3 \longrightarrow NO + O_2 + NO_2\\ NO + NO_3 \longrightarrow 2NO_2\end{array}\right\} \qquad (2)$$

The attack of nitric oxide on nitric acid was believed to become important in the continuing reaction.

Johnston and his collaborators[5a,b] studied the reaction with various, somewhat low, partial pressures of nitric acid, but with the total pressure made up with an inert diluent, such as nitrogen, to near atmospheric pressure. At 300°, heterogeneous reactions took place, and, above 400°, the conversion of nitrogen dioxide to nitric oxide produced complications. At, and just below, 400°, the reaction was homogeneous, and the process (3) was sufficiently slow, compared with the process (1), not to interfere with observation of the earlier part of (1):

$$2NO_2 = 2NO + O_2 \qquad (3)$$

Under these conditions, the initial reaction rates were proportional to the first power of the concentration of nitric acid. The continuing reactions showed retardation by the produced nitrogen dioxide, according to a law which indicated a preliminary, rate-controlling, reversible step, yielding nitrogen dioxide. The retardation was quite analogous to that of the unimolecular solvolysis of alkyl halides by the produced halide ions, except that, here, the retarding agent being a radical, the rate-controlling reversible step had to be a homolytic, and not a heterolytic, dissociation. So, the authors proposed the unimolecular homolytic mechanism (4):

$$\left.\begin{array}{r}HNO_3 \underset{b_2}{\overset{a_1}{\rightleftharpoons}} HO\cdot + NO_2\\ HO\cdot + HNO_3 \underset{c_2}{\longrightarrow} H_2O + NO_3\\ NO_2 + NO_3 \text{ interact as in (2) above}\end{array}\right\} \qquad (4)$$

If k_1 is the observed specific rate, $-dx/xdt$, of the decomposition, and if a_1, b_2, and c_2 are the first- or second-order rate constants of the elementary steps, as shown in eqns. (4), then the kinetic equation which the mechanism requires, and which the data support,[5b] is (5):

$$\frac{1}{k_1} = \frac{1}{2a_1}\left\{1 + \frac{b_2}{c_2}\cdot\frac{[NO_2]}{[HNO_3]}\right\} \qquad (5)$$

The initial specific rate is $k_1 = 2a_1$. The Arrhenius activation energy was 40 kcal./mole.[5a] It is implied that the hydroxyl–nitroxyl bond is much the weakest bond of the nitric acid molecule. Turning their attention to low pressures, the authors found that, at quite low total pressures (*e.g.*, *ca.* 1 mm.), the constant a_1 was proportional to the pressure, and this effect they plausibly interpreted as the second-order limit of a unimolecular reaction. They attempted to reconcile Fréjaques's results on the same basis, but their own experiments at the relevant pressures were complicated by an incompletely understood side-reaction.[5c] Recently, Harrison, Johnston, and Hardwick examined the decomposition of nitric acid at temperatures above 800° in a shock tube. Under these conditions, they were able spectroscopically to recognise the transiently produced nitrogen trioxide.[5d]

(1.2) *The present work.* Obviously, we had to check the kinetics, and the conclusions as to mechanism to be drawn from them, under the conditions which would be used in the intended extension of the study to gaseous aliphatic nitration. In case we should confirm

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[4] Ogg, *J. Chem. Phys.*, 1947, **15**, 337.

[5] (*a*) Johnston, Foering, Tao, and Moserly, *J. Amer. Chem. Soc.*, 1951, **73**, 2319; (*b*) Johnston, Foering, and Thompson, *J. Phys. Chem.*, 1953, **57**, 390; (*c*) Johnston, Foering, and White, *J. Amer. Chem. Soc.*, 1955, **77**, 4208; (*d*) Harrison, Johnston, and Hardwick, *ibid.*, 1962, **84**, 2478.

the unimolecular homolytic mechanism (4), we had to determine the rate constant, a_1, of its rate-controlling step under these conditions; for it was to be expected that the same step would be rate-controlling for unimolecular homolytic nitration.

We studied the decomposition of nitric acid at somewhat low partial pressures (10—48 mm.), but at much larger total pressures (commonly 680 mm.) made up with nitrogen. The temperatures were 303·5 and 349·5°. We examined the kinetics in four reaction vessels as follows, and continued work with the first three of them: (*a*) a Pyrex vessel with a surface/volume ratio (s/v) of 0·7 cm.$^{-1}$; (*b*) a packed Pyrex vessel with $s/v = 1{\cdot}4$ cm.$^{-1}$; (*c*) a silica vessel with $s/v = 0{\cdot}6$ cm.$^{-1}$; and (*d*) a Pyrex vessel internally coated with Fluon, and having $s/v = 0{\cdot}7$ cm.$^{-1}$. We used two methods of following the decomposition, *viz.*, the manometric method and infrared analysis.

In applying the manometric method, we computed the progress of the decomposition of nitric acid from the pressure change, assuming the stoicheiometry of eqn. (1). The final pressures, attained after long periods of reaction, were greater than would be calculated by means of eqn. (1). We attributed the ultimate excess of pressure to partial decomposition of nitrogen dioxide, in accordance with eqn. (3) On Johnston's evidence, and on our own as subsequently obtained, reaction (3) is sufficiently slow, compared with reaction (1), to allow us to neglect both it and the supplementary modes of destruction of nitric acid by the nitric oxide that it produces, over the initial period of the decomposition of the nitric acid. We therefore used the manometric method for two purposes only, *viz.*, first to find convenient conditions for following the fully homogeneous decomposition, having regard to the planned extensions to the nitration of alkanes, and, secondly, to determine for ourselves, particularly in view of previous discrepant conclusions, the kinetic order of the initial rate of decomposition of nitric acid under our conditions.

Table 1 summarises the results of runs in which the manometric method was used. Thus, the 27 runs of Series A were carried out at 303·5° in the unpacked Pyrex vessel. When the logarithms of the initial rates, derived from the pressure–time curves, were plotted against the logarithms of the initial partial pressures of nitric acid, in order to obtain the " order " of the initial reaction in nitric acid, a straight line of slope 1·1 was obtained. Taking this to signify linear dependence in simplest principle, the initial rates were plotted against the initial partial pressures, in order to obtain the first-order rate constant. The plot was linear, and the constant had the value 0·0064 sec.$^{-1}$. All of this is summarised in the first row of Table 1; the other rows similarly summarise the results of the other five series of runs.

The runs of Series A and B show that, at 303·5°, an important part of the reaction in Pyrex vessels is heterogeneous, *ca.* 39% of it in the unpacked reaction vessel (*a*), and *ca.* 56% in the packed one (*b*). From the rates and the s/v ratios of these reaction vessels, one can compute the homogeneous rate, as shown in Table 1.

TABLE 1.

Decomposition of nitric acid vapour in nitrogen at a total pressure of 680 mm.
Initial rates by the manometric method.

Runs	Temp.	Partial pressures HNO_3 (mm.)	Reaction vessel Surface	s/v (cm.$^{-1}$)	Initial " order " in HNO_3	Initial k_1 (sec.$^{-1}$)
A, 1—27	303·5°	10—48	(*a*) Pyrex	0·7	1·1	0·0064
B, 1—7	,,	14—48	(*b*) Pyrex	1·4	0·9	0·0089
				Homogeneous rate, extrapolated:		0·0039
C, 1—6	349·5	15—42	(*a*) Pyrex	0·7	1·0	0·041
D, 1—7	,,	14—48	(*b*) Pyrex	1·4	1·1	0·039
					Mean:	0·040
E, 1—7	303·5	27—43	(*c*) Silica	0·6	1·0	0·0074
F, 1—2	,,	40, 45	(*d*) Fluon	0·7	—	0·0118

The runs of Series C and D show that, at 349·5°, the surface reaction in the Pyrex vessels, even in the packed one, has become undetectably small. We subsequently made this our standard temperature, and accepted the reaction vessels (*a*) and (*b*) as satisfactory for work at this temperature.

We did, however, look into the possibility of working at the lower, in some ways more convenient, temperature 303·5°, by the use of other reaction vessels. As the runs of Series E show, the silica vessel (*c*) was found to be not quite as good as the Pyrex vessel (*a*), though it was better than the packed Pyrex vessel (*b*), in the matter of minimising the heterogeneous reaction at this temperature. At 349·5°, there was nothing to choose between the three vessels (*a*), (*b*), and (*c*), and we used them all in subsequent work. The Fluon-lined vessel (*d*), tested in the runs of Series F, was clearly inferior, and was not used further.

Throughout these experiments, the uniform result emerged, as Table 1 shows, that the " order " of the initial rate of decomposition with respect to the substrate is first, and not second.

TABLE 2.

Run G 4, in the Pyrex reaction vessel (*b*) (s/v = 1·4 cm.$^{-1}$) at 349·5°, with an initial nitric acid pressure of 32·3 mm., and a total pressure, made up with nitrogen, of 680 mm.

(1) *Measured pressures of nitric acid in the infrared cell*

Time (t_1 sec.)	1	2	3	5	10	20	30	60	90	120	180	240
HNO_3 (mm.)	10·9	10·45	10·55	9·7	9·3	7·95	7·25	5·95	4·55	3·85	2·85	2·0

Pressures in the reaction vessel, at the moment of expansion of its contents into the cell, were greater than those here listed by the common factor 32·3/11·2. (The figure 11·2 is obtained by extrapolation of the pressures listed above.)

(ii) *Smoothed pressures* (*in cell*), *their rates of change* (*per sec.*), *and the specific rates* (k_1) *in sec.*$^{-1}$)

t (sec.)	$[HNO_3]$ (mm.)	$[NO_2]$ (mm.)	$[NO_2]_{calc.}$ (mm.)	$\frac{-d[HNO_3]}{dt}$	10^2k_1	$\frac{[NO_2]_{calc.}}{[HNO_3]}$
0	11·2	0·0	0·0	0·280	2·50	0·000
5	10·0	1·2	1·2	0·182	1·82	0·120
10	9·18	2·1	2·02	0·148	1·61	0·220
20	8·00	3·25	3·2	0·095	1·20	0·400
30	7·21	4·0	4·0	0·075	1·04	0·555
40	6·58	4·65	4·62	0·058	0·88	0·70
50	6·03	5·2	5·17	0·046	0·76	0·855
60	5·57	5·6	5·63	0·040	0·72	1·01
70	5·14	6·0	6·06	0·0326	0·63	1·18
80	4·81	6·25	6·39	0·0256	0·53	1·33
90	4·54	6·5	6·66	0·0260	0·571	1·47
110	4·01	7·0	7·19	0·0245	0·610	1·79
130	3·54	7·5	7·66	0·0215	0·606	2·16
150	3·19	7·9	8·01	0·0180	0·565	2·52

Even though the initial rates were obtained from the pressure–time curves by means of a method (Section 3.3) calculated to minimise subjective errors, we could not feel at all satisfied with their absolute accuracy, because it was made all the more difficult to detect systematic errors of extrapolation, owing to care which we were taking to standardise every item of experimental and computational procedure. Therefore it seemed that we had no recourse but to go over to chemical analysis, and thus to study the continuing reaction sufficiently to allow an extended portion of the reaction–time curve to contribute to the determination of the initial specific rate.

We decided on infrared analysis, because we could thus measure directly and fairly accurately the most important concentration variable, *viz.*, the concentration of nitric acid, which in all previous work had not been directly measured, but had been deduced from measured concentrations of nitrogen dioxide, assuming the stoicheiometry of eqn. (1). From the infrared spectrum, we could measure both the concentration of nitric acid, through its strong hydroxyl stretching fundamental band at 2·83 μ, and the concentration of nitrogen dioxide, through its medium-intensity combination band at 3·47 μ (the strongest of the bands of this molecule which are not overlapped by nitric acid bands). Both measurements depended on direct calibration for band-height in terms of vapour pressure, and, because of the nature of the band envelopes, the calibration for nitric acid was the more accurate. We did find that, over a large part of the reaction, the sum of the measured concentrations of nitric acid and of nitrogen dioxide was constant to within the accuracy of the latter measurement, as would follow from eqn. (1), provided that reaction (3) has not yet supervened. Over this part of the reaction, we thought that we could obtain slightly more accurate values of the concentration of nitrogen dioxide by using the measurement of nitric acid concentration and the stoicheiometry of eqn. (1), than we could obtain by direct measurements of nitrogen dioxide, although, as a matter of routine, we made both measurements.

A series of " runs," with different initial pressures of nitric acid, and under constant initial conditions otherwise, were carried out by this method. What we shall now call a " run," really consisted of a number of independently started experiments, in which the reaction vessel was charged with identical initial pressures of nitric acid and of nitrogen, and then, after time intervals which were increased in the successive experiments, the contents of the reaction vessel were expanded into the infrared cell. Each experiment thus provided one analytical sample. From the succession of infrared analyses, we obtained pressures of nitric acid, and of nitrogen dioxide, as functions of the time of reaction. The pressures thus recorded were those in the infrared cell; however, they were connected, by a common factor, with the pressures in the reaction vessel at the moment of expansion of its contents into the cell. From curves of the analytical data, we could thus obtain smoothed pressures and rates of change of pressure of nitric acid, and of nitrogen dioxide, as functions of time; and, from these, we could calculate specific rates of reaction, $k_1 = -d[HNO_3]/[HNO_3]dt$, as a function of the retardation parameter $[NO_2]/[HNO_3]$ of eqn. (5). Thus, we could test eqn. (5), and, in so far as it was valid, evaluate its constants a_1 and b_2/c_2. Then, by carrying out other " runs," *i.e.*, collections of experiments, with other initial partial pressures, we could test the constancy of the constants a_1 and b_2/c_2. We first illustrate the procedure with Run G 4 in Table 2 and Fig. 1. As Fig. 1 shows, k_1^{-1} is a linear function of the product/factor ratio, represented by $[NO_2]/[HNO_3]$, up to a ratio of unity, *i.e.*, to 50% reaction. Between ratios 1 and 1·5, *i.e.*, 50—60% of reaction, this relation becomes inaccurate, and at larger times it is completely out of accord with the data. This is a general finding: all the runs show these effects. They mean, as we shall show, that, at about 50% of reaction, a new accelerating influence is beginning to become important which counteracts the retarding effect of nitrogen dioxide, and prevents k_1^{-1} from rising further as the reaction continues.

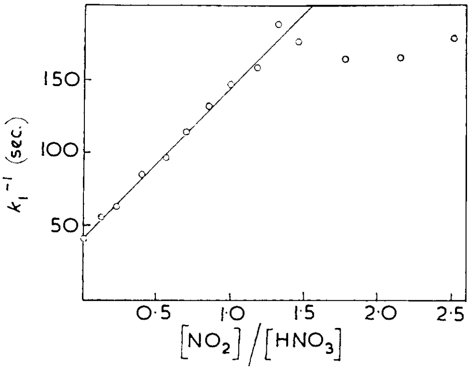

FIG. 1. Gaseous decomposition of nitric acid in nitrogen at 349·5°, at a total pressure of 680 mm. Plot of the reciprocal of the specific rate against the product/factor ratio.

We have considered how far these effects could be due, not to the incursion of a new reaction which destroys nitric acid, but to those changes of gas composition in the reaction vessel which would result from the nitrogen dioxide, formed in reaction (1), having, in the later parts of runs, become partly decomposed, in accordance with reaction (3). We should not find such a subsequent decomposition by means of our analyses, because any nitric oxide, formed in the reaction vessel, would combine with oxygen at the lower temperature of the infrared cell, and so would be measured as its equivalent of nitrogen dioxide. However, in the reaction, the concentration of nitrogen dioxide, and hence the retardation parameter $[NO_2]/[HNO_3]$, would be smaller than we have been assuming. Thus, in a diagram such as Fig. 1, the points belonging to late times, *i.e.*, those lying towards the right, would become shifted leftward, if a correction for this difference of composition in the reaction and in the infrared cell would be applied. Moreover, those points which lie most towards the right would be shifted most towards the left, and thus the whole series of points, which diverge strongly from the linear curve, might become concentrated more closely towards the curve.

Ashmore and Burnett [6] have recently described the kinetics of reaction (3), and have elucidated its mechanism. The reaction involves several steps, and the kinetics require three rate constants or ratios of such in order to describe them. They determined all three quantities as functions of temperature. We have used their data in order to compute, by a method described elsewhere by one of us,[7] how much nitrogen dioxide formed in reaction (1), assumed to obey the kinetic law (5), would be decomposed by reaction (3), obeying Ashmore and Burnett's kinetic law, under the conditions of our experiments, at certain of the late times for which we record rates and analytical compositions. That is, we have computed by how much certain points, such as those most towards the right in Fig. 1, have to be shifted horizontally to the left, in order to correct for the difference, arising from reaction (3), between the gas composition in the reactor at the time of sampling and that in the infrared cell at the time of analysis. The results are significant. Points on or nearly on the rectilinear curve required no appreciable displacement. Points markedly to the right of the curve required leftward shifts by amounts roughly proportional to the horizontal displacements of the points from the curve. However, these calculated displacements are only *ca.* $\frac{1}{4}$—$\frac{1}{3}$ of the size they would have to be in order to bring the points on to the curve.

The meaning seems clear. The kinetic disturbance, which occurs after 50% of reaction, is indeed dependent on the production of nitric oxide by reaction (3). But the effect comprises, not only a composition disturbance, such as would be corrected by the horizontal displacement, calculated as described above, of the aberrant points, but also a rate of disturbance, to correct for which a succeeding upward displacement of the points would be required. As nitric oxide appears, a new mode of destruction of nitric acid must set in, which makes an increasing contribution to the rate as decomposition proceeds further. Presumably, this is a reaction between nitric oxide and nitric acid. Reactions of this kind have been assumed by Fréjaques,[3] and also by Johnston and his collaborators,[5c] in explanation of certain kinetic effects observed by them at low total pressures.

It is evident, however, that eqn. (5), corresponding to the homolytic unimolecular mechanism (4), governs all that part of the decomposition of nitric acid from which the linear plot, illustrated in Fig. 1, derives. We may use such a plot in order to determine the initial specific rate of the decomposition, $k_1 = 2a_1$, and hence the important rate constant, a_1, of the dissociation, which constitutes the first and rate-controlling step of mechanism (4). The intercept and slope of the line in Fig. 1 measure, respectively, $1/2a_1$ and $(b_2/c_2)/2a_1$, as these quantities are given by the run G 4. The values of a_1 and of b_2/c_2, similarly derived from all the runs of Series G, are contained in Table 3. The initial first-order rate constant, k_1 for the decomposition at 349·5°, is simply $2a_1$, and its mean value is 0·025 sec.$^{-1}$.

From the figures of Series G in Table 3, it will be seen that the casual error is considerable. The analytical error in a single determination should be within about 0·3 mm., but the effect of such an error may become considerably enlarged in the computational

[6] Ashmore and Burnett, *Trans. Faraday Soc.*, 1962, **58**, 253.

[7] Godfrey, Ph.D. Thesis, London, 1963, Appendix 2.

processes which lead to a_1, and even more enlarged in those which lead to b_2/c_2. Thus, two analytical errors, of the magnitude mentioned, in adjacent readings, if they happened to be of the same sign, would often be enough to account for the deviations of the poorer individual values from the overall means.

In order to ascertain whether the total pressure, 680 mm., provided a sufficiently rapid means of energy distribution to secure that the unimolecular decomposition of nitric acid was being studied well within the pressure region of first-order kinetics, and that we were not on, or very near, the edge of the Lindemann fall-off of the rate, which then goes finally into second-order kinetic form at sufficiently low pressures, we performed a single " run " at the much lower total pressure 230 mm., with the results shown in the last line of Table 3.

TABLE 3.

Runs of Series G and H. Rate constants and rate-constant ratios of elementary steps in the unimolecular homolytic mechanism of gaseous decomposition of nitric acid in nitrogen at 349·5°.

Run	Initial $[HNO_3]$ * (mm.)	Reaction vessel		10^2a_1 (sec.$^{-1}$)	b_2/c_2
		Surface	s/v (sec.$^{-1}$)		
		Series G.—Total pressure 680 *mm.*			
G 1	33·2	(*c*) Silica	0·6	1·09	2·0
G 2	26·9	,, ,,	,,	1·30	4·0
G 3	37·9	,, ,,	,,	1·44	3·0
G 4	32·3	(*b*) Pyrex	1·4	1·22	2·5
G 5	26·2	,, ,,	,,	1·39	4·0
G 6	29·5	,, ,,	,,	1·12	2·5
G 7	16·5	(*a*) Pyrex	0·7	1·32	3·0
G 8	40·8	,, ,,	,,	1·12	2·0
				Mean: 1·25	Mean: 2·9
		Series H.—Total pressure 230 *mm.*			
H 1	30·0	(*a*) Pyrex	0·7	1·22	8·0

* Pressure in reaction vessel.

The unimolecular rate constant a_1 was the same as before to within the experimental error. This confirms that our rates of dissociation, measured at 680 mm. pressure, are not being disturbed by an insufficient rate of energy redistribution. It also shows that we are well protected by such a high pressure of nitrogen against disturbances of temperature, arising from the endothermicity of the reaction. One of the purposes of having a gaseous medium which is inert is to provide a heat reservoir, in which the rate-controlling homolysis can proceed at a constant temperature, despite the endothermicity of the over-all reaction. Evidently we are fulfilling this requirement.

The increased value of b_2/c_2 at the lower total pressure is worthy of more study than we have given it. The increase is nearly 3-fold, for the 3-fold reduction of pressure. This suggests that the attack by hydroxyl on the hydrogen atom of nitric acid is much more dependent on third-body participation than is the recombination of hydroxyl with nitrogen dioxide. Perhaps the hydroxyl " hammer " needs an " anvil " in order to strike with effect at so mobile an atom in the nitric acid molecule as is its hydrogen atom.*

(2) *The Gaseous Nitration of Alkanes, Particularly Methane.*—(2.1) *Previous work.* In the period 1936—1949, Hass and his co-workers [8] recorded many studies of the products

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* Its easiest evasive movement, rotation round the HO–N bond, meets a barrier of only 10 kcal./mole much less than any bond-strength.[7a]

[7a] Cohn, Ingold, and Poole, *J.*, 1952, 4272.

[8] Hass, Hodge, and Vanderbilt, *Ind. Eng. Chem.*, 1936, **28**, 339; (*b*) Hass and Paterson, *ibid.*, 1938, **30**, 67; (*c*) Seigl and Hass, *ibid.*, 1939, **31**, 648; (*d*) Hibsham, Pearson, and Hass, *ibid.*, 1940, **32**, 427; (*e*) Hass, Dorsky, and Hodge, *ibid.*, 1941, **33**, 1138; (*f*) Hass and Riley, *Chem. Rev.*, 1943, **32**, 376; (*g*) Hass, *Ind. Eng. Chem.*, 1943, **35**, 1146; (*h*) Hass and Howe, *ibid.*, 1946, **38**, 251; (*i*) Hass and Schechter, *ibid.*, 1947, **39**, 817; (*j*) Hass and Alexander, *ibid.*, 1949, **41**, 2266.

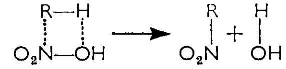
of the gaseous nitration of alkanes by nitric acid and by nitrogen dioxide. The former reagent was the faster acting, but both gave the same products, *viz.*, all the mononitro-compounds that could be formed by inserting a nitro-group in place of any hydrogen atom or any lower alkyl group in the alkane, and all the aldehydes and ketones that could result from oxygen uptake where hydrogen or a lower alkyl group had been split off, together with various products of their further oxidation. The order of ease of replacement of the different types of hydrogen atom was: tertiary > secondary > primary. No rearrangement of the carbon skeleton was observed.

One of the theories of mechanism considered [8b, 9] during this work was that free radicals, thermally produced from the nitrating agent, or from unstable oxidation products, attack the alkane to produce an alkyl radical, which engages in a chain reaction (6):

$$\left.\begin{array}{l}\mathrm{RH + Initiator \longrightarrow R\cdot + (?)}\\ \left.\begin{array}{l}\mathrm{R\cdot + HNO_3 \longrightarrow RNO_2 + \cdot OH}\\ \mathrm{RH + \cdot OH \longrightarrow R\cdot + H_2O}\end{array}\right\}\text{chain}\end{array}\right\} \qquad (6)$$

Combination of nitrogen dioxide with the methyl radical was assumed to be a main means of chain-termination. Degradation of hydrocarbon chains was presumed to occur, after the alkyl radical had been converted to an olefin.

Somewhat later,[8f, g] Hass took into consideration what was described as an " addition complex " mechanism. It was bimolecular, proceeding through a four-centre " complex," as illustrated for attack on a C–H bond in eqn. (7).



$$\begin{array}{c}\mathrm{R{-}H}\\ \vdots\quad\vdots\\ \mathrm{O_2N{-}OH}\end{array} \longrightarrow \begin{array}{c}\mathrm{R}\qquad\mathrm{H}\\ |\;+\;|\\ \mathrm{O_2N}\quad\mathrm{OH}\end{array} \qquad (7)$$

An analogous mode of attack on C–C bonds was envisaged, but this, in our view, was a less fruitful suggestion, to which we shall not refer again.

Still later, Bachman, Hass, and their co-workers [10] supported the radical-type mechanism which they particularised as in (8), allowing that additional steps were possible:

$$\left.\begin{array}{l}\mathrm{HNO_3 \longrightarrow HO\cdot + NO_2}\\ \mathrm{RH + HO\cdot \longrightarrow R\cdot + H_2O}\\ \mathrm{R\cdot + NO_2 \longrightarrow RNO_2}\end{array}\right\} \qquad (8)$$

One of their chief arguments was that the reaction proceeded in the gas phase. Even though this was before the altered thinking, consequent on Maccoll's demonstration of heterolytic gas reactions, had taken place, it was a curious prejudging of the question for decision—a kinetic question needing an answer from kinetics. They [10] made the interesting suggestion that alkyl radicals combine with nitrogen dioxide to form, in part, alkyl nitrites, which, at the temperatures used, decompose quickly, in the known way, to a carbonyl compound and a lower alkyl radical:

$$\mathrm{R_3'C{\cdot}ONO \longrightarrow R'\cdot + R_2'CO + NO} \qquad (9)$$

It was shown in Part I [2] that skeletal rearrangement does occur in a gaseous nitration, which could go by way of a free alkyl radical in which rearrangement would be expected. This unequivocally supports a radical mechanism of the type (6), leaving open, of course, the possible concurrence of a molecular mechanism of the type (7).

Both Fréjaques and Johnston examined the kinetic effect of methane on the gaseous decomposition of nitric acid. Fréjaques,[3] using somewhat low pressures, found that the nitric acid disappeared up to 1·5 times faster when excess of methane was introduced He found that the initial rates, and the continuing rates, had kinetic orders between 1 and 2

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[9] McCleary and Degering, *Ind. Eng. Chem.*, 1938, **30**, 64.

[10] (*a*) Bachman, Hass, Addison, Hewett, Kohn, and Millikan, *J. Org. Chem.*, 1952, **17**, 906; (*b*) Bachman, Atwood, and Pollack, *ibid.*, 1954, **19**, 312; (*c*) Bachman and Standish, *ibid.*, 1961, **26**, 570.

with respect to nitric acid. He assumed that nitrogen dioxide and nitrogen trioxide, formed as in eqns. (2), attack the methane, so producing methyl radicals, which combine with nitrogen dioxide. Johnston,[5b] using nitrogen at much higher total pressures, reported briefly that the rate of gaseous decomposition of nitric acid was changed by no more than a factor of two or three on addition of an excess of methane. He assumed mechanism (8).

Schay, Giber, and their collaborators [11a] measured the rate of production of nitromethane, and of nitric oxide, from nitric acid and methane in nitrogen at 280—490°. Giber and Meisel examined the products.[11b] Nitration and oxidation occurred in the constant ratio of 35 : 65, though the formed nitromethane subsequently decomposed, with the result that observed conversions to nitromethane were less than 35%, and, measured at successive times, passed through a maximum. The rate of formation of nitromethane was described as proportional to $[HNO_3][CH_4]^{\frac{1}{2}}$. Non-chain and chain mechanisms were considered, which were derived from eqns. (6) and (8), by making the primary homolysis bimolecular with nitrogen or methane:

$$X + HNO_3 \longrightarrow X + HO\cdot + NO_2 \qquad (X = N_2, CH_4) \qquad (10)$$

and by adding further steps. These theories of mechanism predicted a weak dependence of the rate on methane concentration, but not the power one-half. The products were nitromethane, hydrogen cyanide, formaldehyde, formic acid, carbon dioxide, nitrogen dioxide, nitric oxide, and water. Geiseler and his co-workers [12] gave a generally similar picture of the kinetics of the gaseous nitration of ethane. A mechanism based on eqns. (8) was considered, which had added steps to permit the development of a chain process. The suggestion was made that nitroalkanes may thermally decompose in the gas phase by way of an isomerisation to transiently formed alkyl nitrites.

(2.2) *Nitration of methane. Results.* The reaction between nitric acid and methane was followed in the gas phase at 349·5° by the method of infrared analysis, as used in the preceding study of the decomposition of nitric acid alone. Each " run " was a group of successive experiments, started with identical concentrations of all the substances involved, and continued for successively increasing lengths of time before the contents of the reaction vessel were expanded into the infrared cell, each such experiment thus provided one timed sample, and one point in the composition–time curve of the " run." In nearly all the runs, the reaction vessel was the unpacked Pyrex vessel (*a*) ($s/v = 0{\cdot}7$ cm.$^{-1}$), but a control run was performed with the packed vessel (*b*) ($s/v = 1{\cdot}4$ cm.$^{-1}$) in order to confirm the homogeneity of the reaction. The essential analytical measurement was of nitric acid concentration, through the intensity of its absorption band at 2·83 μ. We could not measure the nitrogen dioxide concentration, because the band at 3·47 μ, on which we relied in the previous investigation, was now overlapped; however, we did find, in the weak band at 5·6 μ, a means to follow qualitatively the larger changes of concentration undergone by nitrogen dioxide.

As to initial conditions, methane was introduced in large excess over the nitric acid. When, as in most runs, the sum of the pressures of these two substances was less than 700 mm., the total pressure was made up to this value with added nitrogen. Whereas, over the experiments of a run, all initial partial pressures were kept the same, the partial pressures of nitric acid and methane were varied from run to run.

The partial pressures of nitric acid, measured at successive times, in a number of runs, are recorded in Table 4. Each figure represents a separate experiment, but may be the mean of several analyses of the same sample. The disappearance of nitric acid now has a kinetic form entirely different from that observed in the absence of the methane. Over a considerable first portion of any run, about 40—60%, the plot of the logarithm of the

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[11] (*a*) Schay, Giber, Tamás, and Soos, *Magyar Kém. Folyóirat*, 1959, **65**, 311; (*b*) Giber and Meisel, *Acta Chim. Acad. Sci. Hung.*, 1960, **22**, 455.

[12] (*a*) Geiseler and Reinhardt, *Z. Elektrochem.*, 1957, **61**, 296; (*b*) Geiseler and Ratzsch, *Z. Phys. Chem.* (*Frankfurt*), 1960, **26**, 131.

TABLE 4.

Runs, Series M, of the reaction between nitric acid and methane in the Pyrex reaction vessel (*a*) ($s/v = 0{\cdot}7$ cm.$^{-1}$) (one run in the packed vessel (*b*), s/v 1·4 cm.$^{-1}$) at 349·5°, and at a total pressure of 700 mm., made up with nitrogen. Pressures of nitric acid as a function of time.

Run: M...	1	2	3	4	5	6	7	8	9	10	11 ‡	12	13	14
$[HNO_3]_0$ *	14·7	14·7	14·7	19·3	5·0	9·7	14·7	16·2	19·8	22·7	10·95	5·0	7·45	9·7
$[CH_4]_0$ * ...	89	337·5	525	684	89·5	97·5	97·5	97·5	97·5	97·5	97	701	698	696
t (sec.)	$[HNO_3]_t$ †													
2	5·1	4·82	4·9	6·1	1·72	2·9	4·7	5·15	6·33	7·2		1·56	2·33	3·01
3		4·7		5·75	1·57	2·95	4·45	5·05	6·0	6·7	3·4	1·45	2·26	2·91
4	4·55	4·55	4·4	5·0	1·50	2·7	4·3	4·9	5·7	6·2		1·40	2·05	2·70
5		4·1	4·05	4·1	1·53	2·7	4·1	4·65	5·2			1·29	1·93	2·58
6	4·4	4·2	3·8	3·55	1·43	2·65	3·95	4·4	4·9	5·3	3·0	1·22	1·85	2·48
7		3·75			1·35	2·4	3·8		4·65				1·66	
8	4·1	3·67	3·35	2·65				3·75		4·5				
9					1·27	2·25	3·5				2·65			
10	3·6	3·2	2·6							3·35				
11					1·21	2·1	3·3							
12	3·35	2·8		1·5						2·7	2·4			
13					1·10		2·7							
14	2·7	2·65												
16	2·4	2·3												
19		1·8												
22		1·5												

* Initial pressures in the reaction vessel, in mm., at 349·5°. † Pressures, in infrared cell, of samples taken at times *t*, in mm., at 20°. ‡ Run in the packed reaction vessel.

partial pressure of nitric acid against the time is linear, as illustrated for run M 2 in Fig. 2. We see no incursion here of a growing retardation by a product, as is found when nitric acid decomposes alone; in particular, there is no retardation by nitrogen dioxide, although this substance is observed to accumulate, as the nitric acid becomes destroyed.*

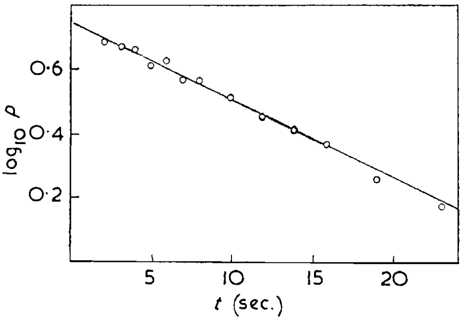


FIG. 2. Run M 2. Gaseous reaction of nitric acid with methane in nitrogen at 349·5°, at a total pressure of 700 mm. Initial pressures in the reaction vessel: $[HNO_3] = 14{\cdot}7$ mm.; $[CH_4] = 337$ mm. Plot of the logarithm of the pressure of nitric acid, in the infrared cell, against the time at which the sample was taken.

Beyond the limit of the exponential reaction, the semi-logarithmic curves lose their linearity, becoming steepened by the entry of some acceleration effect, presumably due to an attack by one or more of the reaction products on nitric acid.

At about the same period as that in which this acceleration enters, an analytical complication manifests itself. Up to then, an analytical sample, once taken, could be analysed at any reasonable time, because the spectrum remained constant. However, at these later times, the spectrum of a sample in the infrared cell changed with time in a way which indicated that nitric acid was being destroyed by some reaction which was proceeding at room temperature in the cell. The nitric acid band at 2·83 μ became progressively

* After the nitric acid has all been destroyed, some slower reaction continues with the consumption, eventually complete, of the nitrogen dioxide that had previously accumulated.

weaker, and a band at 6·2 μ, which might have belonged either to nitrogen dioxide or nitromethane, or both, became strengthened. The obvious deduction, that this reaction was heterogeneous, was confirmed by packing the interior surfaces of the sides of the cell with cleaned glass-wool, when the change proceeded considerably faster. Our way of coping with this effect was to record the spectrum as soon as possible (usually 2 min.) after the sample was taken, and then to record it several times more at regular intervals (usually 2 min.), thus obtaining the data for an extrapolation, which we treated as linear, to give the spectrum as it would have been at the moment of taking the sample. It is difficult to feel sure that the correction, often in the region 10—20% on the first measurement of nitric acid concentration, was adequate. The nature of the disturbing process is unknown; some many-stage reactions start rapidly, and then continue much more slowy and uniformly; and a fast start would be easy to miss. It is possible that some at least of the acceleration, affecting the later parts of runs, may be due to an inadequacy in our correction for the continuing reaction in the infrared cell.

TABLE 5.

First-order rate constants (k_1 in sec.$^{-1}$) of disappearance of nitric acid by reaction with methane in nitrogen at 349·5° and a total pressure of 700 mm.

Run	$[HNO_3]_0$ *	$[CH_4]_0$ *	10^2k_1	Run	$[HNO_3]_0$ *	$[CH_4]_0$ *	10^2k_1
M 5	5·0	89·5	3·86	M 8	16·9	97·5	4·07
M 6	9·7	97·5	3·95	M 2	14·7	337·5	5·15
M 11	10·95	97	3·95	M 3	14·7	525	6·18
M 7	14·7	97·5	4·03	M 12	5·0	701	6·09
M 1	14·7	89	4·05	M 13	7·5	698	6·75

* Initial partial pressures in the reaction vessel, in mm.

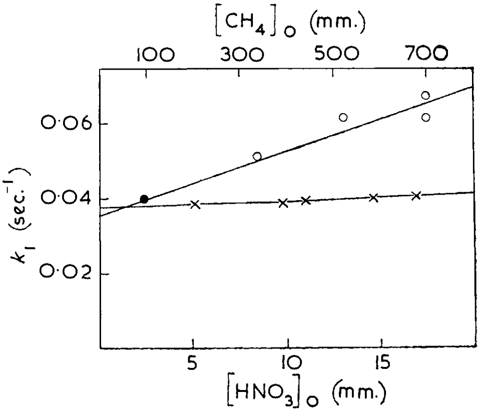


FIG. 3. First-order rate constants for the consumption of nitric acid by gaseous reaction with methane in nitrogen at 349·5°, and at a total pressure of 700 mm. The crosses represent rate constants plotted against the initial pressure of nitric acid, that of methane being held approximately constant (*ca.* 96 mm.). The open circles represent rate constants plotted against the initial pressure of methane. The filled circle marks the position in which one would otherwise have had to put six almost coinciding open circles.

The strength of these disturbances, and the earliness with which they impinged on the kinetic runs, increased generally with increasing initial concentration of the reactants, and was very sensitive to the initial concentration of nitric acid above a certain limit. We found that, with initial pressures of nitric acid above about 18 mm., the accelerative phase, and the reaction in the cell, entered so early and so strongly that reliable first-order rate constants were difficult to obtain. Accordingly, our further conclusions will be based on the data from runs at lower initial concentrations of nitric acid. These runs give satisfactory first-order semi-logarithmic plots. The significant rate constants are given in Table 5.

Their immediate significance is shown in Fig. 3. The almost horizontal straight line shows that the first-order specific rates of consumption of nitric acid are independent of the initial concentration of nitric acid to within the uncertainties of casual and systematic error. The sloping line shows the weak dependence, noted by other workers, of the rate on methane concentration.[11a] The linearity of this curve is not well established, but, assuming linearity, we deduce the limiting specific rate at low methane concentrations to be 0·035 sec.$^{-1}$ at 349·5°. This is appreciably larger than the initial specific rate of decomposition of nitric acid in the absence of methane, *viz.*, 0·025 sec.$^{-1}$ at 349·5°. If the latter rate is regarded as equal to $2a_1$, that is, to twice the rate constant for the elementary step of homolysis of nitric acid, then a_1 is 0·0125 sec.$^{-1}$, and our extrapolated rate of attack on methane for low methane concentrations, is $2{\cdot}8a_1$. The rise in the rate of consumption of nitric acid above this value, as the concentration of methane is increased, is clearly not to be expressed as a kinetic order in the rate as a whole, but it might represent an order in one term of a two-term rate equation, in which the other term is independent of methane concentration.

The kinetic phenomena exhibited by the gaseous reaction between nitric acid and methane, for which we should like to account in a mechanism, are those which appear in our measurements at 349·5° over approximately the first 50% of the consumption of nitric acid, before the additional modes of destruction of nitric acid by the products of this first reaction set in. The main features of this part of the overall reaction are as follows. (1) The consumption of nitric acid by reaction with methane is of first-order with respect to nitric acid. (2) This first-order rate is not retarded by reaction products. (3) It increases slowly with increasing concentration of methane. (4) Its value, extrapolated to low concentrations of methane, is 0·035 sec.$^{-1}$, just a little larger than the initial first-order rate of self-decomposition of nitric acid, namely, 0·025 sec.$^{-1}$, at the common temperature 349·5°. (We say " initial " here, because *this* decomposition *is* retarded by its products.)

(2.3) *Nitration of methane. Conclusions.* The type of mechanism most strongly supported by past work on the products of the gaseous nitration of alkanes is also the type which is at once suggested by the similar values of the specific rate of consumption of nitric acid by reaction with methane and the initial specific rate of self-decomposition of nitric acid. This is the unimolecular, radical type of mechanism, so far illustrated by eqns. (6) and (8); its rate-controlling first step is the homolysis of nitric acid, and is thus the same as the rate-controlling first step of the self-decomposition of nitric acid. For it is certain that the mechanism of the latter reaction is that of eqns. (4).

A general form of the unimolecular, homolytic, alkyl-radical mechanism may be set up by adding to the established equations of the self-decomposition of nitric acid, other equations representing the formation, and all the conceivably important modes of destruction, of methyl radicals. This is done in eqns. (11). Symbols for the rate constants of the elementary steps are added to the equations, and we shall use the same symbols as names for the equations:

$$
\left.\begin{array}{l}
\mathrm{HNO_3} \overset{a_1}{\underset{b_2}{\rightleftharpoons}} \mathrm{HO\cdot + NO_2} \\
\mathrm{HO\cdot + HNO_3} \xrightarrow[c_2]{} \mathrm{H_2O + NO_3} \\
\left.\begin{array}{l}
\mathrm{HO\cdot + CH_4} \xrightarrow[d_2]{} \mathrm{H_2O + \cdot CH_3} \\
\mathrm{\cdot CH_3 + HNO_3} \xrightarrow[e_2]{} \mathrm{CH_3NO_2 + \cdot OH}
\end{array}\right\}\text{chain} \\
\mathrm{\cdot CH_3 + NO_2} \xrightarrow[f_2]{} \mathrm{CH_3NO_2} \\
\mathrm{\cdot CH_3 + HNO_3} \xrightarrow[g_2]{} \mathrm{CH_3{\cdot}OH + NO_2}
\end{array}\right\} \qquad (11)
$$

By making some of the steps in this general scheme much more important than others, we can arrive at various specialised schemes, which have different kinetic characteristics, through which we can check the schemes by the observed kinetic forms, absolute rates, and product compositions.

Any specialised mechanism must include the rate-controlling step a_1, the methyl-radical-forming step d_2, and one of the nitromethane-forming steps, e_2 and f_2. The result that the self-decomposition of nitric acid, represented by steps a_1, b_2, and c_2, is retarded by formed nitrogen dioxide, which engages in step b_2, whereas the reaction with methane is not observed to be so retarded, must mean that, in the latter process, either hydroxyl radicals are being effectively trapped by step d_2, or nitrogen dioxide is being so trapped by step f_2 (which depends on step d_2), or both of these things are happening. In any case, it is clearly unnecessary to take further account of step b_2. Which of the steps e_2 and f_2 should be included, and whether either of the steps c_2 and g_2 should be, are matters which we may hope to decide by comparing with observational results the kinetic consequences of the mechanisms that can be constructed by using the possibilities left open. This we shall now proceed to do. Two kinds of mechanism can be constructed, according as step e_2 is excluded or included. In the former case, they are non-chain mechanisms, and in the latter, chain mechanisms.

There are four non-chain mechanisms. The simplest is mechanism (i), already expressed in eqns. (8):

$$\text{Steps } a_1 + d_2 + f_2. \qquad \text{Rate} = a_1[\text{HNO}_3]. \qquad \text{(i)}$$

If we allow the possibility that the slow increase of specific rate with methane concentration may be due to a concurrent mechanism, this rate equation is acceptable in form. However, it is unacceptable with respect to its predicted rate constant, $a_1 = 0{\cdot}0125$ sec.$^{-1}$ at 349·5, which is too small by a factor of 2·8.

Two further non-chain mechanisms, *viz.*, mechanisms (ii) and (iii), may be considered together:

$$\text{Steps } a_1 + c_2 + d_2 + f_2. \qquad \text{(ii)}$$

$$\text{Rate} = a_1[\text{HNO}_3]\left(\frac{2c_2[\text{HNO}_3] + d_2[\text{CH}_4]}{c_2[\text{HNO}_3] + d_2[\text{CH}_4]}\right).$$

$$\text{Steps } a_1 + d_2 + f_2 + g_2. \qquad \text{(iii)}$$

$$\text{Rate} = a_1[\text{HNO}_3]\left(\frac{2g_2[\text{HNO}_3] + f_2[\text{NO}_2]}{g_2[\text{HNO}_3] + f_2[\text{NO}_2]}\right).$$

These rate equations contain factors expressing retardations of specific rate, which would grow as the runs continue. We do not observe such retardations. The equations have a second shortcoming, namely, that, although they provide absolute rates larger than those of mechanism (i), the increase could never be as large as 2-fold, whereas we need an increase of 2·8-fold in order to fit the experimental data.

One other non-chain mechanism, *viz.*, mechanism (iv), remains to be considered:

$$\text{Steps } a_1 + c_2 + d_2 + f_2 + g_2. \qquad \text{(iv)}$$

The rate equation is too long to print, as it is unacceptable. It contains a factor of progressive retardation which is stronger than either of those in mechanisms (ii) and (iii), and consequently is much too large to have been overlooked experimentally. The equation could provide a large enough initial rate, but only at the expense of providing much less nitromethane than we know to be formed. A successful rate equation must take care of products as well as rates. So this mechanism, and thus all non-chain mechanisms, can be dismissed.

Therefore, we turn to chain mechanisms. The propagation steps are d_2 and e_2. The possible termination steps are c_2, f_2, and g_2. We consider first mechanism (v), which includes step c_2:

$$\text{Steps } a_1 + c_2 + d_2 + e_2. \qquad \text{(v)}$$

$$\text{Rate} = a_1[\text{HNO}_3]\left(2 + \frac{d_2[\text{CH}_4]}{c_2[\text{HNO}_3]}\right).$$

This mechanism appears to be able to provide a large enough rate, and an increase in rate with increasing methane concentration; but these apparent successes are illusory. If the ratio d_2/c_2 is so set as to provide the right absolute rates near the left-hand end of the sloping curve in Fig. 3, it will predict a slope more than twice as great as that observed. No value of d_2/c_2 will take care of both the slope of the curve and its height above the axis of abscissae. A second grave difficulty with this rate equation is that its methane-dependent factor is also a factor of progressive specific acceleration in the course of a run. Thus the points near the right-hand end of the sloping curve in Fig. 3 would have to represent mean values of specific rates, which so rose during the runs that their methane-dependent parts (approximately one-half of the total specific rates) became doubled as the nitric acid concentration fell to one-half of its initial value in the measured and kinetically significant part of the runs. Such a deviation from first-order behaviour could not have been overlooked experimentally. This mechanism can therefore be dismissed.

We next consider termination by step f_2. In the previous literature, this has been considered to be the closing step in both non-chain and chain mechanisms. The chain mechanism i (vi):

$$\text{Steps } a_1 + d_2 + e_2 + f_2. \qquad \text{(vi)}$$

$$\text{Rate} = a_1[\text{HNO}_3]\left(1 + \frac{e_2[\text{HNO}_3]}{f_2[\text{NO}_2]}\right).$$

This rate equation is completely unacceptable, because of its extremely powerful factor of progressive retardation. The runs would start " infinitely " fast, and would soon be going quite slowly. This is contrary to the observations.

Termination by step g_2 seems not to have been considered in the previous literature, but we now take it into account in mechanism (vii):

$$\text{Steps } a_1 + d_2 + e_2 + g_2. \quad \text{Rate} = a_1[\text{HNO}_3]\left(2 + \frac{e_2}{g_2}\right). \qquad \text{(vii)}$$

This is an acceptable rate equation, provided that we are prepared to entertain a separate explanation of the slow increase of rate with increasing methane concentration, *e.g.*, that the increase is the effect of a concurrent bimolecular mechanism, of the type of eqn. (7), which is unimportant unless the concentration of methane is quite large. First, the rate equation of mechanism (vii) is of the correct first-order form. Secondly, by taking the partition ratio e_2/g_2 as 0·8, we obtain the correct rate constant, $2{\cdot}8a_1$. Thirdly, we must ascertain whether this partition ratio provides an acceptable product composition. It requires that 4/9, or 44%, of the methane which reacts will be converted into nitromethane, and that 56% of it will be converted into oxidation products. Schay *et al.*[11a] found that, with due allowance made for the slow decomposition of first-formed nitromethane, 35% of the methane which reacts is converted into nitromethane. However, what we have been calling " nitromethane " in our theoretical discussion, and denoting by " CH_3NO_2 " (not " $CH_3{\cdot}NO_2$ ") in eqns. (11), includes concurrently formed methyl nitrite, which, being unstable at the temperature of the experiments, would appear as extra oxidation products. Thus our calculated 44% might plausibly represent the concurrent formation of 35% of real nitromethane and 9% of methyl nitrite. This seems to be the first suggestion that alkyl radicals, in attacking nitric acid molecules at their weakest point, combine in comparable degree with either the nitroxyl or hydroxyl moiety, and that this is a main cause why the homolytic nitration of alkanes by nitric acid is always accompanied by their oxidation. Hass's occasional recovery of alcohols from gaseous nitrations of alkanes [8f,g] is consistent with this proposal. In this chain reaction with methyl radicals, the chains are quite short, averaging $(e_2 + g_2)/g_2 = 1{\cdot}8$ cycles. The ratio in which the methyl radicals, or any similarly acting alkyl radicals, on breaking the nitric acid molecule, combine with either moiety determines at once the chain-length, the rate constant, and the product composition.

We must work through the remaining chain mechanisms, in order to see if any others can be formed which are consistent with the observations. Four mechanisms, (viii)—(xi), remain to be considered:

Steps $a_1 + c_2 + d_2 + e_2 + f_2$. (viii)

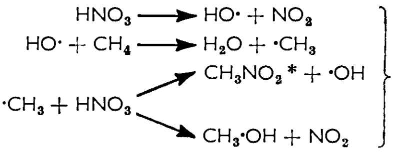
Steps $a_1 + c_2 + d_2 + e_2 + g_2$. (ix)

Steps $a_1 + d_2 + e_2 + f_2 + g_2$. (x)

Steps $a_1 + c_2 + d_2 + e_2 + f_2 + g_2$. (xi)

We do not set down the corresponding rate equations, because they are long, and are unsuccessful in reproducing the experimental findings. For mechanisms (ix), (x), and (xi), we should soften this rejection by remarking that it depends essentially on our ability to detect a progressive diminution of specific rate, and is therefore only definite to the extent allowed by our experimental precision. These three mechanisms are elaborations of the basic mechanism (vii), being made either by allowing hydroxyl radicals to be trapped, not only by methane, but also, to some extent, by nitric acid [mechanism (ix)], or by allowing methyl radicals to be trapped, not only by nitric acid, but also in part by nitrogen dioxide [mechanism (x)], or by allowing both of these second branch-paths to carry some proportion of the material [mechanism (xi)]. All that we can assert, on the basis of our results, is that the second branch-paths must, by about an order of magnitude at least, carry less material than the corresponding main branch-paths, *i.e.*, those taken to be the sole paths in mechanism (vii).

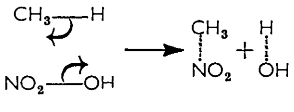
We now recapitulate the descriptions of mechanism to which we have been led. The primary gaseous reaction between nitric acid and methane has a main, unimolecular homolytic mechanism, and a minor concurrent, bimolecular mechanism. The main mechanism is a radical-chain process. Its steps are identified by first developing the theory of such processes, in the stages described, represented by eqns. (6) and (8), and finally (11), and then particularising the general theory by the criterion of the new experimental results. Thus we arrive at eqns. (12):



$$\left.\begin{array}{l} HNO_3 \longrightarrow HO\cdot + NO_2 \\ HO\cdot + CH_4 \longrightarrow H_2O + \cdot CH_3 \\ \cdot CH_3 + HNO_3 \longrightarrow CH_3NO_2{}^{*} + \cdot OH \\ \cdot CH_3 + HNO_3 \longrightarrow CH_3\cdot OH + NO_2 \end{array}\right\} \qquad (12)$$

* Includes $CH_3\cdot NO_2$ and $CH_3\cdot ONO$.

The minor mechanism is derived from a historical origin in eqn. (7), but, in contradistinction to this original suggestion, is here pictured as proceeding, without the intermediate formation of an addition compound, in a single bimolecular step, which probably has heterolytic character, as illustrated in eqn. (13):



$$CH_3{-}H + NO_2{-}OH \longrightarrow CH_3{-}NO_2 + H{-}OH \qquad (13)$$

We consider that our data are consistent with, but do not prove, these mechanistic descriptions. We did once hope to end with a fully proved mechanism, but as it gradually became clear that a more comprehensive attack would be needed to attain this goal, we made it our reduced objective to apply the techniques we had in order so to expose the problem as to determine the requirements of an adequately organised attack. The main needs are to follow the concentration changes, not only of nitric acid, but also of nitromethane and nitrogen oxides, and to establish with precision the functional form of the methane-dependent part of the rate. One might hope to meet the first of these requirements with more versatile analytical arrangements. The second requirement is one of accuracy, and is made severe by the smallness of the methane-dependent part of the rate.

We have made preliminary experiments, employing propane in place of methane, in order to see whether the hydrocarbon-dependent part of the rate of reaction with nitric acid could be so enlarged, by the use of a homologue of methane, that the functional form of the dependence could be established with accuracy, and without the need to go up to such high concentrations of hydrocarbon that all, or nearly all, of the diluent nitrogen becomes replaced. We feel sure that the problem can be solved in that way, and the experiments are being continued.

EXPERIMENTAL

Materials.—The nitric acid was freshly purified before each run, in a branch of the vacuum line, by twice distilling it from sulphuric acid at a low temperature and pressure, the nitric acid being condensed at the temperature of liquid nitrogen. It was degassed by pumping the solid, just thawing it, and pumping again. Occasionally, the solid nitric acid turned red during pumping. The red colour vanished when the liquid-nitrogen bath was removed, and could not be brought back by recooling. Whether the acid had been red or not seemed to make no difference to its chemical-kinetic properties. Red hydrochloric acid has been described before,[13] but not red nitric acid. Lattice imperfections are a possible cause.

Methane, as purchased, was free from homologues and from hydrogen, but contained 3—4% of carbon dioxide, and a few tenths % of oxygen and nitrogen. It was freed from carbon dioxide and oxygen, and finally from moisture, by conventional means, and its purity was checked by means of gas chromatography.

Apparatus.—The thermostat was an electrically wound cylindrical aluminium block (dia., 25 cm.; height, 40 cm.), provided with thermoregulator and thermocouple, and a central hole (dia., 10 cm.) into which the reaction vessel fitted. The hole was closed above and below with thick aluminium plugs.

The reaction vessels, one unpacked of Pyrex ($s/v = 0{\cdot}7$ cm.$^{-1}$), one of Pyrex packed with Pyrex tubing ($s/v = 1{\cdot}4$ cm.$^{-1}$), and one unpacked of silica, were all of about 700-ml. capacity. Exit tubes led to an optical pressure-gauge (diaphragm type), a mixing bulb of 5-l. capacity (itself connected to an optical pressure-gauge), and a sampling bulb of about 500-ml. capacity (as large as this in order to make negligible the " dead-space " in connecting tubes), which was in connexion, though a ground joint, with an infrared cell. The whole vacuum line was evacuated by using a mercury-diffusion pump, backed by a two-stage oil pump. All taps which came into contact with nitric acid were greased with Florube W grease, and all other taps with Apiezon M grease.

The infrared cell (dia., 4 cm.; length, 10 cm.) had silver chloride windows. Using Teflon O-rings and Florube grease, vacuum-tight joints were made between the windows and the rest of the cell. It was used in a Grubb–Parsons Gs2A spectrometer.

Kinetic procedure–pressure measurements. In order to start a run, freshly purified nitric acid was first evaporated to the required pressure into the previously evacuated mixing bulb, and then nitrogen was admitted to make a total pressure of 740 mm. Because of the speed of the runs, it was not useful to open the tap to the previously evacuated reaction vessel for an indefinitely long time in order to charge the vessel to pressure equilibrium. Our procedure was to open the tap for a standard time, depending on the temperature, the time being 1·0 sec. in runs at 349·5°. Using nitrogen, a calibration curve was constructed relating initial pressures (*ca.* 740 mm.) in the mixing bulb to the pressures (*ca.* 680 mm.) which were set up in the reaction vessel by this method. The latter pressure proved to be a constant fraction of the former. The casual error involved was not more than 0·5 mm.

The reaction vessel having been charged with nitric acid and nitrogen, a number of timed pressure readings were taken. The initial rate of change of pressure was determined from the graphed results by means of the Gregory–Newton method of extrapolation. This initial rate was converted to an initial rate of reaction by assuming the stoicheiometry of eqn. (1). This method was not used in runs involving hydrocarbons.

Infrared analysis. This method was used both for the self-decomposition of nitric acid, and for its reactions with methane, and with propane. When a hydrocarbon was to be used, the charging procedure involved supplying nitric acid to the required pressure in the mixing bulb as before, then the hydrocarbon to the required pressure, and then making up the total

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[13] Johnston and Martin, *J. Chem. Phys.*, 1952, **20**, 534.

pressure with nitrogen. The gas mixture was expanded into the reaction vessel as before. In some runs, the charge was thus put into the reaction vessel in two approximate " halves," the second " half " containing all the nitric acid. This modification of method was tried in expectation of reducing any " warming-up " error, but this error may have been negligible, for we are not able to say that we noticed any effect of the procedural modification.

In this method, a sample had to be withdrawn, each experiment providing only one timed sample. A set of experiments with constant initial concentrations, and different times of sampling, constituted a " run." Again, because of the speed of the reactions, the tap from the reaction vessel to the sampling bulb, with which the infrared cell was in connexion, was opened for the standard time, 1·0 sec. As in the charging of the reaction vessel, so in this sampling process, the pressure was not in equilibrium (it could not be, because in the reaction vessel the reaction was still going on, which changes the pressure), but the pressure produced in the infrared cell by this procedure was a constant fraction of the pressure in the reaction vessel. We did not have to establish this by a special calibration, because it was given by the results themselves. Over the experiments of a run, the analytical results gave the pressure of nitric acid in the infrared cell as a function of the time at which the sample was taken, and, from that, the pressure at zero time could be deduced. This, together with the initial pressure of nitric acid in the reaction vessel for that run, gave the pressure ratio. It was found to be the same for all initial pressures of nitric acid, that is, for all runs.

The infrared analyses were based on *ad hoc* calibration. Nitric acid was measured by using the height of its band at 2·83 μ. In order to obtain the calibration curve, nitric acid at various pressures, 0—20 mm., measured by means of the optical-diaphragm gauge to 0·1 mm., was put into the cell, and nitrogen was then added to make the total pressure 265 mm., which is about the pressure produced when a sample is taken from the reaction vessel. The spectrum around 2·8 μ was recorded, and the peak-height was measured with a travelling microscope. The analytical error was about 0·3 mm. of nitric acid.

In experiments on the self-decomposition of nitric acid, nitrogen dioxide was measured by using its medium-intensity band at 3·47 μ. Pure dinitrogen tetroxide was prepared, and the gas from this, a mixture of dinitrogen tetroxide and nitrogen dioxide, was put into the cell. From the total pressure of this mixture, and the equilibrium constant of Giauque and Kemp,[14] the composition was calculated, and hence what the pressure would have been if none of the nitrogen dioxide had been dimerised, was deduced. This pressure was correlated with the peak-height of the band, and so a calibration curve for nitrogen dioxide was built up. The error was about 0·3 mm. of nitrogen dioxide.

In each experiment, the sample was taken, its infrared spectrum was recorded, and the measured peak-heights were converted to partial pressures by means of the calibration curves. In some experiments, the spectrum had to be recorded repeatedly at timed intervals, as explained in Section 2.2. In the experiments of each run, the initial pressure of nitric acid (10—40 mm.) was constant to within 0·1 mm., and that of methane to *ca.* 0·5 mm., whilst the total pressure was constant to 2 mm.

In the experiments on the nitration of methane (and propane), the nitrogen dioxide concentration could not be followed, because the band at 3·47 μ was heavily overlapped. A large development or disappearance of nitrogen dioxide could be qualitatively followed by means of the intensity changes around 5·6 μ.

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[14] Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 50.