[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO[1]]

The Kinetics of Nitration of Aromatic Nitro Compounds in Sulfuric Acid[1]

BY F. H. WESTHEIMER AND M. S. KHARASCH

I. Introduction

The kinetics of the nitration of aromatic nitro compounds in sulfuric acid solution has been studied with a view toward elucidating the mechanism of the reaction. In conformity with the pioneer work of Martinsen,[2] it was found that the second order reaction between aromatic nitro compounds and nitric acid has a maximum rate in about 90% sulfuric acid. More precise investigation of the conditions for maximum rate showed that it occurred at a definite acidity (defined by Hammett's H_0 function) rather than at a definite concentration of sulfuric acid. This discovery in turn strongly suggested that an ionization of the nitric acid was involved in the determination of the maximum. The most probable ionizations are

$$HNO_3 + H_2SO_4 \longrightarrow H_2NO_3^+ + HSO_4^- \quad (1)$$
$$HNO_3 + 2H_2SO_4 \longrightarrow H_3O^+ + NO_2^+ + 2HSO_4^- \quad (2)$$
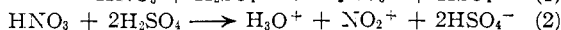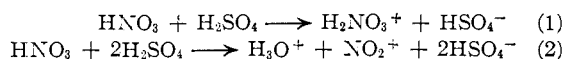
Ionizations of indicators which parallel both the type of ionization shown in equation 1 and that shown in equation 2 were investigated. It was shown that an ionization of the type shown in equation 2 (and not that shown in equation 1) will account for the thousand-fold increase in rate

(1) This investigation of the kinetics of nitration in concentrated sulfuric acid was part of the work carried on for the National Defense Research Committee under contract OD-9 (NDCrc-4). The work was completed in the summer of 1941 and transmitted in a confidential report to NDRC. No further theoretical studies of the nitration process in sulfuric acid were carried out for NDRC, but a very extensive series of investigations was later reported by Bennett and his co-workers in England. The English scientists (who had received a copy of our report) set forth a great deal of interesting and significant original work, which not only confirmed our principal conclusions but refined and greatly amplified them. Their work overlapped ours only with respect to one significant matter; they also performed experiments showing the effect of bisulfate ion on the reaction rate (see ref. 11). This paper has been prepared in such a way that it does not prejudice the publications which Bennett and his co-workers are now making.

(2) Martinsen. Z. physik. Chem., **50**, 385 (1905); **59**, 605 (1907). See also Klemenc and Scholler. Z. anorg. Chem., **141**, 231 (1924).

of nitration which accompanies an increase in sulfuric acid concentration from 80 to 90%; it follows therefore that the active nitrating agent in sulfuric acid is NO_2^+.

It should be noted that this work, although sufficiently precise to support the statements above, is not of the highest accuracy; in general the speed with which the work could be accomplished was considered of first importance.

II. The Kinetics of Nitration

The reaction between aromatic nitro compounds and nitric acid in concentrated sulfuric acid solution is bimolecular and the rate is unaffected by traces of nitrous acid. The rate of nitration of half a dozen nitro compounds proved to be about three times as great in 95 as in 100% sulfuric acid.[2] Lauer and Oda[3] found that a similar situation obtained for the nitration of anthraquinone. The study of the nitration of hydrocarbons in sulfuric acid is complicated by the fact that the reaction is heterogeneous.

In a significant experiment, Martinsen[2] added 50 g. of phosphorus pentoxide to 250 cc. of 95% sulfuric acid. The nitration proceeded at the same rate as in the absence of the phosphoric anhydride. Obviously, the dehydrating power of the sulfuric acid is not the determining factor in the rate of nitration. On the contrary, the present work has shown that the determining factor for nitration in sulfuric acid is the acidity of the medium.[4] The concept of acidity in "superacid" solutions can be understood in terms of the H_0 function, introduced by Hammett and his co-workers.[5] This function is a logarithmic measure of acidity, equal to pH in dilute aqueous solutions of acids; in superacid solutions it ac-

(3) Lauer and Oda, J. prakt. Chem., **144**, 176 (1936).

(4) Hammett, "Physical Organic Chemistry." 1940, p. 313; THIS JOURNAL, **50**, 2666 (1928).

(5) Hammett and Deyrup, ibid., **54**, 2721 (1932).

quires a negative value and for 100% sulfuric acid is approximately equal to −10.6. The value of the H_0 function can be determined by a colorimetric method, employing those indicators which have an uncharged basic form and a single positive charge in the acid form.

One mole per liter of potassium acid sulfate reduces the acidity of 85% sulfuric acid about 0.12 log unit, a change just about equal to the effect of a mole per liter of water. (The latter would reduce the concentration of 85.00% sulfuric acid to 84.15%, lower the H_0 function by 0.12 unit.) Nitrobenzene lowers the acidity of sulfuric acid more than twice as much, per mole, as does water. Phosphorus pentoxide and dinitrobenzene do not have large effects upon the acidity of sulfuric acid.

III. Kinetic Results

The bimolecular rate constant for the nitration of nitrobenzene has been measured at 25° in dilute solution in moderately concentrated sulfuric acid. The data for the rate constants, determined at varying concentrations of sulfuric acid, with and without potassium acid sulfate, are recorded in Table I and in Fig. 1.

TABLE I

RATE CONSTANTS FOR THE NITRATION OF NITROBENZENE AT 25°

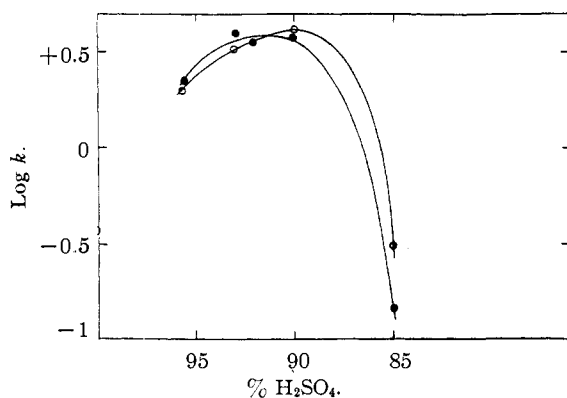| Expt.	H₂SO₄, %	C₆H₅NO₂	HNO₃	KHSO₄	k, min.⁻¹ (m./l.)⁻¹
1	95.6	0.02	0.02		1.96
2	95.6	.01	.01		2.20
6	93.0	.02	.02		3.2
3	92.0	.02	.02		3.4
4	90.0	.01	.01		4.1
5	85.0	.02	.02		0.31
10	82.5	.05	.05		.013
7	80.0	.04	.04		.0014
9	95.6	.02	.02	0.46	2.2
11	93.0	.02	.02	.46	3.9
12	92.0	.02	.02	.46	3.3
13	90.0	.02	.02	.46	3.7
8	85.0	.02	.02	.70	0.14

Fig. 1.—Nitration rate of nitrobenzene with and without potassium acid sulfate: O, no KHSO₄; ●, KHSO₄ (about 0.5 m./l.).

It is clear that the rate of nitration goes through a maximum at around 90% sulfuric acid. It is noteworthy that the rate of nitration in 80% sulfuric acid is only 1/3000 of the rate in 90% acid.

Further, addition of bisulfate increases the rate in solutions more concentrated in sulfuric acid than 90%, and lowers the rate in solutions of less than 90% sulfuric acid. This behavior is understandable on the basis of the hypothesis that the maximum rate occurs at a definite value of H_0, the acidity, rather than at a definite composition of acid. Then, since bisulfate lowers the acidity, it will cause a decrease in rate when the acidity is less than the optimum but an increase in rate when the acidity is already greater than the optimum. This conclusion is at least semi-quantitatively in agreement with the effect that bisulfate has on the H_0 function.

The effect of other materials on the nitration of nitrobenzene is recorded in Table II. To these data we can add Martinsen's observation that the rate is unchanged by phosphorus pentoxide.

TABLE II

EFFECT OF ADDED MATERIALS ON THE RATE OF NITRATION OF NITROBENZENE AT 25°

Expt.	H₂SO₄	Compound added (A)	C₆H₅NO₂	HNO₃	A	k, min.⁻¹ (m./l.)⁻¹
4	90		0.01	0.01		4.1
15	90	m-C₆H₄(NO₂)₂	.02	.02	0.36	3.3
5	85		.02	.02		0.31
17	85	NH₂SO₃H	.02	.02	.012	.27
18	85	HSO₃NO₂	.02	.02	.013	.28
14	85		.60	.02		.12
7	80		.04	.04		.0014
16	80		.02	.97		.0046

The materials, such as dinitrobenzene and phosphorus pentoxide, which do not materially affect the acidity of the medium have no appreciable effect upon the rate. Nor does the small quantity of sulfamic acid (which removes oxides of nitrogen) or trace of nitrosylsulfuric acid change the nitration velocity.[6] It has already been shown, however, that nitrobenzene lowers the acidity of the medium. When used in large excess, the absolute rate, of course, is increased but the rate constant is decreased, corresponding to a decrease in acidity. Large quantities of nitric acid increase the rate constant for nitration in solutions of 80% sulfuric acid. It will be shown later that in solutions more acid than that which corresponds to the optimum conditions, nitric acid (presumably by lowering the acidity) again increases the rate constant.

The maximum rate of nitration occurs in slightly more acid solution as the temperature is raised. The optimum conditions correspond to 89% at 5°, 90 at 25° and 91 at 40°. The maximum also becomes more diffuse the higher the temperature, especially on the side involving the more concentrated acid.

(6) Bennett later showed that large quantities of nitrosylsulfuric acid do depress the nitration rate.

TABLE III

NITRATION OF NITROBENZENE AT 5 AND 40°

Expt.	T, °C.	H₂SO₄	Concentration, moles/liter C₆H₅NO₂	HNO₃	k, min.⁻¹ (m./l.)⁻¹
34	5	95.6	0.04	0.04	0.22
29	5	93.0	.02	.02	.40
31	5	90.0	.04	.04	.55
32	5	87.5	.02	.02	.33
35	5	86.5	.04	.04	.125
25	40	96.5	.02	.02	8.4
22	40	93.0	.01	.01	10.0
24	40	91.5	.01	.01	10.4
23	40	90.0	.01	.01	11.5
26	40	87.5	.02	.02	5.6
27	40	85.0	.02	.02	0.87
28	40	82.5	.02	.02	.098

The nitration of other nitro compounds was carried out to determine whether the position of the maximum rate was influenced by the structure of the nitro compound. Clearly it is not. The rates of nitration of dinitromesitylene and of dinitroxylene also show a maximum with changing sulfuric acid concentration, and the maxima

TABLE IV

THE RATE OF NITRATION OF DINITROMESITYLENE AT 25°

Expt.	H₂SO₄	Concentration C₆H₂(CH₃)₃ (NO₃)₂	HNO₃	k, min.⁻¹ (m./l.)⁻¹
38	95.6	0.02	0.02	0.62
41	91.5	.01	.01	1.1
39	90.0	.02	.02	1.4
42	88.5	.01	.01	0.74
40	85.0	.01	.01	.16

TABLE V

THE RATE OF NITRATION OF DINITRO-m-XYLENE AT 50°

Expt.	H₂SO₄	Concentration, moles/liter (CH₃)₂C₆H₂ (NO₂)₂	HNO₃	k, min.⁻¹ (m./l.)⁻¹
56	100.1	0.48	0.08	0.035
58	100.1	.51	1.01	.069
50	95.6	.02	0.02	.046
53	93.0	.02	.40	.18
57	93.0	.09	.09	.16
51	90.0	.02	.40	.085

Included in Table V is an experiment carried out with a high concentration of nitric acid in 100% sulfuric acid. The concentration of sulfuric acid exceeds that in which the maximum nitration rate occurs. The rate at low nitric acid concentration is only a quarter of the maximum rate; at high nitric acid concentration, it is almost half of the maximum. Nitric acid decreases the acidity of 100% acid (see Section IV), thereby bringing the acidity closer to the optimum value, and increasing the rate constant.

Table VI contains some miscellaneous estimates of nitration rates.

The activation energy for the nitration of nitrobenzene in 90% sulfuric acid, calculated from the data presented in Tables I and II, is around 15,000 cal./mole. The rate of nitration of p-nitrotoluene at 100° and 90% sulfuric acid is much too fast to measure. On the basis, however, of the reasonable assumption that the effects of temperature and of acid concentration are approximately the same for the nitration of p-nitrotoluene as for nitrobenzene, the rate constant for the former under any conditions can be estimated. The nitration rate for p-nitrotoluene calculated in this manner, is about 10^7 as great as that of 2,4-dinitrotoluene (at 100° and in 90% sulfuric acid). In this instance, the introduction of a second nitro group into an organic molecule has decreased the nitration rate by a factor of ten million; if this large factor is general, it would explain the ease with which preparative reactions of nitration can be directed to yield products containing exclusively one, or two, or three nitro groups as desired.

It is realized, of course, that in commercial operations solubility effects complicate the kinetic data. The solubility of a nitro compound increases with the percentage of sulfuric acid, and to maintain a high concentration of the nitro compound in solution (to obtain the maximum rate) it will be necessary to operate in solutions more concentrated in sulfuric acid than would be necessary merely to obtain the maximum rate constant.

TABLE VI

ESTIMATES OF THE RATES OF NITRATION OF SOME AROMATIC COMPOUNDS

Expt.	T, °C.	H₂SO₄, %	Compound	Nitro compound	HNO₃	k, min.⁻¹(m./l.)⁻¹
19	25	80.0	p-C₆H₄CH₃NO₂	0.01 m./l.	0.01 m./l.	0.42
59	25	82.5	m-C₆H₄CH₃NO₂	.02	.02	3.2
60	25	82.5	o-C₆H₄CH₃NO₂	.02	.02	7.5
61	25	82.5	p-C₆H₄CH₃NO₂	.02	.02	3.9
45	25	85.0	C₆H₅CH₂CO₂H	.02	.02	3.9
4	25	90.0	HO₃SC₆H₄CH₂CO₂H	.02	.02	8.0
62	100	95.6	CH₃C₆H₃(NO₂)₂	.12	.12	0.023
63	100	90.0	CH₃C₆H₃(NO₂)₂	.12	.12	.021

are in the same region where the rate of nitration of nitrobenzene would show a maximum at the same temperature. Further, the shape of the acidity-rate curve is the same for all these simple nitro compounds.

IV. The Ionization of Nitric Acid

The cryoscopic studies of Hantzsch[7] and of

(7) Hantzsch, Z. physik Chem., **61**, 257 (1907); **65**, 41 (1908); Hammett and Dryrup, THIS JOURNAL, **55**, 1900 (1933); Treffers and Hammett, ibid., **59**, 1708 (1937).
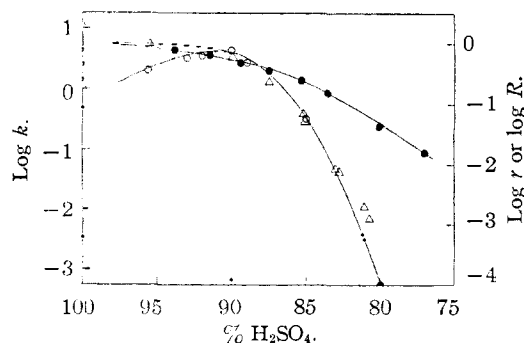
Fig. 2.—Comparison of nitration rate and ionization of anthraquinone and trinitrotritanol: $\log k$ = O (nitration rate); $\log r$ = ● (anthraquinone); $\log R$ = △ (trinitrotritanol).

Hammett[7] show that nitric acid ionizes in sulfuric acid solutions, and that the number of particles produced for each molecule of nitric acid approaches four. The ionization can only involve the action of nitric acid as a base toward the sulfuric acid, and the number of particles produced suggests that the mode of ionization shown in equation (2) is correct. In order to investigate the matter, it was necessary to find indicators which would ionize in the manner shown for nitric acid in both equations (1) and (2); furthermore, to make the comparison convincing, the conversion of the indicator from the basic to the acid form should occur in sulfuric acid of a concentration similar to that in which nitration takes place (*i.e.*, 80 to 100% sulfuric acid).[7a] It was possible to find such indicators. In the first place, anthraquinone, one of Hammett and Deyrup's[5] indicators, ionizes in a manner parallel to that shown in equation (1), and is half converted to its acid form in 89.7% sulfuric acid.

$$HNO_3 + H_2SO_4 \longrightarrow H_2NO_3^+ + HSO_4^- \quad (1)$$
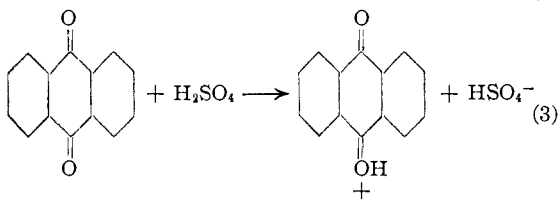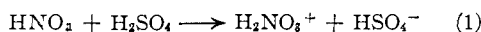
Since triphenyl carbinol gives a four-fold freezing point depression in sulfuric acid solution, four particles must be formed from each molecule of this compound when it is dissolved in the acid.[7] Moreover, the sulfuric acid solutions of triphenylcarbinol are colored, and there are good reasons to ascribe the color to the triphenylcarbonium ion.[8] Consequently, for the work to be described, there was needed a triphenylcarbinol derivative which would be converted into the colored carbonium ion in the neighborhood of 90% sulfuric

(7a) This approach was suggested in conversation by Professor L. P. Hammett.

(8) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

acid, the concentration of acid which produces the maximum nitration rate. Such a derivative was found in p,p',p''-trinitrotriphenylcarbinol (hereafter called trinitrotritanol) which (by analogy with triphenylcarbinol) ionizes as follows

$$(O_2NC_6H_4)_3COH + 2H_2SO_4 \longrightarrow$$
$$(O_2NC_6H_4)_3C^+ + H_3O^+ + 2HSO_4^- \quad (4)$$
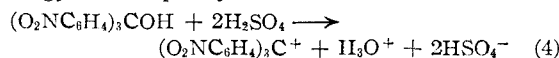
This exactly parallels the second of the proposed ionizations of nitric acid

$$HNO_3 + 2H_2SO_4 \longrightarrow H_3O^+ + NO_2^+ + 2HSO_4^- \quad (2)$$
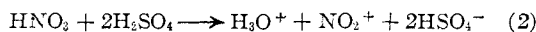
The fractions of the two indicators which are present in any solution in the colored forms were determined colorimetrically. The fraction, r, represents the ratio of the concentration of the oxonium ion of anthraquinone ion to the sum of the concentration of this ion and the concentration of un-ionized anthraquinone, whereas the fraction, R, represents the ratio of the concentration of trinitrotriphenylcarbonium ion to the sum of the concentration of this ion and trinitrotritanol. The logarithms of k, r and R have been plotted in ·Fig. 2 against the concentration of sulfuric acid. It is clear from this graph that the ionization of anthraquinone is unrelated to the other two functions. On the other hand, the close parallel between the logarithm of the fraction (R) of trinitrotritanol in the ionized form and the logarithm of the rate of nitration (k) is excellent evidence that the two processes depend upon the same type of ionization. The parallel is the more striking because of the enormous change in rate (over a thousand-fold) which accompanies a 10% change in the acid concentration. The change in color of a simple indicator (anthraquinone) over the same range is only twelve-fold.

The curves for the ionization of trinitrotritanol and for the rate of nitration deviate from one another both in the weakest and in the strongest acid employed. The deviation in the weak acid solutions is probably due to an experimental error in the determination of the amount of ionization of the carbinol where this amount is very small; the cause of this error is explained in the experimental section. The deviation on the strongly acid side is, however, real. The ionization of the trinitrotritanol approaches a definite upper value, whereas the rate of nitration passes through a maximum. A plausible explanation of this maximum has been advanced by Bennett and his co-workers.[9]

Experimental

Colorimetric Determinations.—The colorimetric measurements were made with a Bausch and Lomb colorimeter. The trinitrotritanol[10] after many recrystallizations from benzene, melted at 194–193.5° (cor.). The material was still slightly yellow, but its solutions in 50% sulfuric acid were almost colorless. Since this indicator dissolves in 90% sulfuric acid, solutions in that solvent were used. It was found, however, that these solutions are not stable.

(9) Bennett, Brand, James, Saunders and Williams, in press.

(10) E. Fischer and O. Fischer, *Ber.*, **37**, 3355 (1904).

After standing for an hour or more at room temperature, they develop a yellow color, which persists in 50% sulfuric acid. For this reason, all the measurements here made were carried out with freshly prepared and cooled solutions of the indicator.

In concentrated sulfuric acid solutions, the reproducibility of color is good; in more dilute solutions, however, the indicator in question is not completely reliable. In 81% acid, for example, where only about a thousandth of the indicator is in the colored form, a slight amount of yellow decomposition product would account for a considerable error.

The colorimetric method developed by Hammett and Deyrup[5] was employed to determine the effect of various compounds on the acidity of sulfuric acid solutions. Here anthraquinone was employed as an indicator.

Kinetic Measurements.—The rate of nitration was in most cases measured calorimetrically.[11] The method depends only on measuring the temperature rise as a reaction proceeds. Nitration is well adapted to the method, since the heat of nitration is large. The temperature rise for 0.02 M solutions of nitro compound and nitric acid in sulfuric acid is about 1°.

In order to conserve time, a non-adiabatic calorimeter was used. This is necessarily less accurate than an adiabatic calorimeter for long experiments, but was sufficiently accurate for the determinations desired. The calorimeter consisted of a 500-cc. Pyrex Dewar which was supported on a cork in a metal can. The can was closed with a metal top, sealed with an oil-resistant rubber gasket, and held down with eight screws. There were openings in the metal top for a stirrer, a Beckmann thermometer, and for the introduction of materials. The stirrer was operated by a synchronous motor, through a pulley system at about 200 revolutions per minute. The entire calorimeter was immersed in an oil thermostat until the oil covered the top by about a centimeter.

The heat of stirring was determined and found to be 0.014° per hour. The coefficient of thermal leakiness, determined for sulfuric acid solutions, was 0.0010°/min.[12]

The solution of the nitro compounds in sulfuric acid was placed in the calorimeter at the required temperature, and the calorimeter placed in the thermostat. The temperature inside was generally maintained a few tenths of a degree under the bath temperature, so that the average temperature during the run would approximate that of the bath. After a steady state had been reached (only temperature changes due to stirring and leakage) a solution of nitric acid in sulfuric acid was introduced. This solution had previously been brought to the temperature of the bath, and was introduced by means of a rapidly emptying pipet which was at the temperature of the bath. Of course, the initial readings were influenced by the change in temperature due to the introduction of the nitric acid solution. Tests showed that this effect was negligible after three minutes.

The temperature read from the Beckmann thermometer was plotted against time. Corrections for stirring and for thermal leakage were made in the usual manner.[12]

It was not easy, however, to obtain the rate constants. The initial temperature could be obtained by extrapolating to the time at which the nitric acid had been introduced. However, the final temperature could not usually be obtained because of the long time the nitration required. After an hour, the errors in the corrections for stirring and leakage were no longer negligible. Furthermore, the rate constant was increasing slowly during the reaction, because of the rise in temperature; toward completion of several of these experiments, it was 7 or 8% higher than initially. These difficulties were overcome by use of successive approximations in conjunction with the method of Roseveare.[13] That investigation showed how the rate con-

stant and final reading (in this case the final temperature rise) could be computed from the data of an individual experiment for a second order reaction, provided the reactants were present in equal concentrations and the observations were made at equal time intervals. His method was not intended to apply, of course, to the case in which the rate constant increased (due to rise in temperature) with time.

When the change in rate constant is small, the following approximate method can be followed. Let

$$dx/dt = Ae^{-E/RT}(a - x)^2 \qquad (5)$$

where x is the concentration of the nitration product formed at time t in the second order reaction, a is the initial concentration of either nitro compound or nitric acid, E is the activation energy and A is a constant. Furthermore

$$T = T_0 + T_i = T_0 + x\theta \qquad (6)$$

where T is the temperature at time t, T_0 is the initial temperature, T_i the temperature increase between the initial time and t, and θ is a constant defined by equation 6. If $x\theta/T_0$ is small, equations 5 and 6 lead to 7 and 8.

$$\frac{dx}{(a - x)^2} - \frac{E\theta}{RT^2}\frac{x\, dx}{(a - x)^2} = k\, dt \qquad (7)$$

$$\frac{x}{a(a - x)} - \frac{E\theta}{RT^2}\left[\frac{x}{a - x} - \ln\frac{a}{a - x}\right] = kT =$$

$$\frac{x}{a(a - x)} - \Delta \qquad (8)$$

The data corrected for heat of stirring and thermal leak (see above) are those which would have been obtained in an ideal calorimeter. The method of Roseveare was applied directly to these data; it yields an approximate value for k and for $a\theta$, the value of the temperature rise which would have been observed at infinite time in the absence of all thermal leak and heat of stirring. The approximate value of θ so obtained could be used to calculate approximate values of x from the observed values of T_i at various times. This permitted the computation of approximate values of Δ. The values of Δ were only about 4%, at most, of $x/a(a - x)$.

The values of the concentration, x', of nitration product which would have been obtained if the rate constant were not a function of temperature were then obtained from equation 9.

$$\frac{x}{a(a - x)} - \Delta = kt = \frac{x'}{a(a - x')} \qquad (9)$$

From the values of x', the corresponding values of T' could be obtained (where T' represents the temperature rise at time t which would have been obtained if the rate constant were not a function of temperature). The method of Roseveare could then be applied to these new data to yield values of k and of $a\theta$ which are more nearly correct. It was then possible to substitute the corrected values of θ in equation 8 and obtain a more precise estimate of Δ. Actually, there was no gain in repeating the approximation method; since the corrections for increase in rate constant during any one experiment were very small, the original approximate corrections sufficed. The average deviations in the corrected values of θ were only a few per cent.

This method of successive approximations is laborious and was actually applied in detail only to experiments 1, 2 and 5. In all other cases, the value of the rate constant was determined by an inexact short-cut. The assumption was made that the value of 39° liter/mole for θ determined in experiments 1, 2 and 5, would hold in all cases. Although this assumption is unquestionably an approximation, it is not responsible for large errors. With this value of θ, it became possible to calculate each rate constant from the initial rate in any experiment. This was advantageous since none of the corrections (stirring, thermal leak, change of k with temperature) had to be applied. The error in rate constant might well be 10%; there is, however, reason to believe (see below) that it is not very much larger. This method (using only the initial rate) was of

(11) Barry, THIS JOURNAL, **42**, 1911 (1920); Sturdevant, *J. Phys. Chem.*, **45**, 127 (1941).

(12) White, "Modern Calorimetry," (Chemical Catalogue Co.) Reinhold Publ. Corp., New York, N. Y.

(13) Roseveare, THIS JOURNAL, **53**, 1651 (1931).

TABLE VII

SAMPLE OF COMPLETE CALCULATION

Experiment #5: Nitration of Nitrobenzene in 85% H₂SO₄ at 25°[a]

Time, min.	T₁, °C Obs.	T₁, °C Net	T₁, °C Cor.[d]	T₂, °C Obs.	T₂, °C Net	T₂, °C Cor.[d]	T₃, °C Obs.	T₃, °C Net	T₃, °C Cor.[d]	aθ, °C 1st approx.	T₁, °C final[f]	T₂, °C final[f]	T₃, °C final[f]	aθ,[b] °C 2nd approx.	k[e], min.⁻¹ (m./l.)⁻¹
0	(3.856)[e]	0.000	0.000	4.124	0.268	0.253	4.279	0.423	0.405	1.02	0.000	0.251	0.400	0.98	0.27
5	3.895	.039	.037	4.144	.288	.273	4.290	.434	.416	1.00	.037	.271	.411	.96	.29
10	3.929	.073	.069	4.162	.306	.290	4.301	.445	.427	1.02	.069	.287	.422	1.00	.26
15	3.957	.101	.095	4.180	.324	.308	4.311	.455	.437	0.96	.095	.305	.432	0.95	.31
20	3.985	.129	.122	4.197	.341	.324	4.320	.464	.446	.95	.122	.321	.441	.93	.33
25	4.010	.154	.145	4.211	.355	.338	4.330	.474	.456	.95	.144	.334	.451	.90	.31
30	4.038	.182	.172	4.228	.372	.354	4.340	.484	.466	.94	.170	.350	.460	.91	.34
35	4.059	.203	.192	4.241	.385	.367	4.348	.492	.475	.93	.190	.362	.469	.92	.33
40	4.082	.226	.213	4.252	.396	.378	4.356	.500	.483	.97	.211	.373	.476	.93	.31
45	4.103	.247	.233	4.266	.410	.392	4.364	.508	.492	.94	.231	.387	.486	.93	.33
										Av. 0.97				Av. 0.94	Av. 0.31
														±0.03	±0.02

[a] Concentration of nitrobenzene = concentration of nitric acid = a = 0.02365 mole/liter. [b] θ = 39.8° liters/mole. [c] k = 0.31 min.⁻¹ (moles/liter)⁻¹. [d] Corrected for heat of stirring and thermal leak. Temperature of thermostat, 25.0°, corresponded to 4.116° on the Beckmann thermometer. [e] Extrapolated. [f] Corrected for heat of stirring, thermal leak, and Δ.

course necessarily used for the very slow nitrations. In general, the present study was concerned with very large differences in rate; the method employed was adequate to support conclusions which rest on these large differences.

The data for one of the experiments for which the computations have been carried through in detail are presented in Table VII. The temperatures recorded in the columns of this table marked T_2 and T_3 are those observed 50 and 100 minutes, respectively, after the corresponding value of T_1 (e. g., the last reading of 4.364° was made one hundred and forty-five minutes from the start of the experiment). The method of Roseveare[13] permits the determination of $a\theta$ and of k from any three observations separated by equal time intervals (here fifty minutes). The values for the first approximation to $a\theta$ were obtained by application of Roseveare's equation 14 to T_1 (cor.), T_2 (cor.) and T_3 (cor.). The small corrections, Δ, for increase in the rate with temperature were then applied as explained above. Then a second approximation to $a\theta$ was obtained by application of Roseveare's equation 14 to the final values (T') of T_1, T_2 and T_3; the values of k were calculated from these temperatures by means of his equation 15. It will be noted that small errors in T_1, T_2 and T_3 (such as may be introduced by errors in approximating the heat of stirring) will change considerably the average deviation of k and $a\theta$ from their respective averages. The internal consistency of the few cases calculated was however satisfactory.

The calorimetric method gave considerable difficulty for the determinations of the rate of nitration of dinitro-m-xylene at 50°. Some determinations were therefore made by measuring the concentration of nitric acid in a nitrometer. Experiments nos. 56, 57 and 58 were made by this means. It is of interest that the rate constant for nitration determined by the nitrometer method for 93% sulfuric acid was 0.16, and that determined by the approximate calorimetric method, 0.18. The rate constants for the few experiments which duplicate those of Martinsen[2] agreed as a first approximation with his. (Our values were a little higher.)

The nitric acid used was usually 70% acid, kept colorless

with a small quantity of sulfamic acid. The experiments with 100% sulfuric or with large quantities of nitric acid were made with 90.5% nitric acid. The sulfuric acid was Baker and Adamson's analytical grade found by titration to be 95.6%. Solutions of 80%, 85%, 90% and 100% were made up, and analyzed. These solutions were found to correspond with the stated percentage within a tenth of a per cent. Other solutions were made up from these by volume. The nitro compounds were distilled or recrystallized and were of good quality. The 4,6-dinitro-1,3-dimethylbenzene was made according to Errera and Maltese[14] and melted at 93–94°.

Summary

1. The kinetics of nitration in sulfuric acid solution of nitrobenzene (and of eight other nitro compounds) were investigated.

2. The rate of nitration is a maximum in 90% sulfuric acid; in the presence of potassium bisulfate, the maximum occurs at a slightly higher concentration of acid.

3. The rate of nitration of nitrobenzene increases by a factor of about 3000 when the concentration of sulfuric acid is increased from 80 to 90%. This increase in rate parallels the ionization of trinitrotriphenylcarbinol in the same media.

4. These facts have been interpreted to indicate that in sulfuric acid solution, the NO_2^+ ion is the effective nitrating agent.

5. Mononitrotoluene nitrates about 10,000,000 times as fast as does dinitrotoluene under the same experimental conditions.

(14) Errera and Maltese, "Beilstein," Vol. V, p. 380.