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Kinetics of Aromatic Nitration in Acetic Anhydride[1]

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The rate of nitration of benzene in acetic anhydride containing 0.4 to 2 *M* nitric acid has been studied at 25°. The reaction is first order in benzene and approximately second order in nitric acid. The observed rate is slowed by a competing reaction between nitric acid and the solvent for which a correction was established. In the presence of 0.01 *M* sulfuric acid, the benzene nitration rate is markedly increased and at the same time becomes proportional to the first power of the nitric acid concentration. Sodium nitrate at 0.001 *M* concentration on the other hand markedly decreases the rate. The results are on the whole consistent with a nitronium-ion mechanism. Dilution of the solvent with 50% by weight of acetic acid has practically no effect on the benzene nitration rate. Further dilution decreases it and in acetic acid itself there is practically no reaction.

Acetic anhydride is widely used as a solvent for the nitration of compounds susceptible to oxidation or hydrolytic attack by aqueous mixed acid. While the mechanism of aromatic nitration for aqueous mixed acid and for nitric acid solutions in a number of other inert solvents is reasonably well established,[3,4] there remains some uncertainty in the case of acetic anhydride. Evidence has been offered for N_2O_5, possibly functioning as nitronium nitrate, as the effective nitrating agent[5] but acetyl nitrate also has been considered to play a major role.[6] The presence of both these species in equilibrium with HNO_3 is suggested by Raman spectra for mixtures of nitric acid with acetic anhydride.[7] Nitronium ion also has been detected in concentrated solutions of nitric acid in acetic anhydride by its infrared absorption.[8]

In the present investigation, kinetic data have been obtained for the nitration of benzene in nitric acid–acetic anhydride solutions at 25°. Previous data for this reaction date prior to the establishment of the nitronium-ion theory[9] and a re-examination in the light of present knowledge seemed desirable.

Experimental

Efforts to prepare completely colorless nitric acid of 100% concentration by vacuum distillation of either fuming nitric acid mixed with concentrated sulfuric acid or sodium nitrate mixed with concentrated sulfuric acid were unsuccessful at temperatures as low as 35°. The product was invariably pale yellow as it entered the condenser. A colorless product containing about 92% HNO_3 was obtained by distilling B. & A. A. C. S. reagent fuming nitric acid under reduced pressure at 40–50° with an air leak at the head of the fractionating column. This acid was stored within a desiccator kept in a refrigerator and remained colorless indefinitely. It was analyzed by acid-base titration with reference to potassium hydrogen phthalate and was used for the preparation of the reaction mixtures. At the highest concentration of nitric acid employed in the rate studies, about 2 *M*, the concentration of water introduced was about 0.6 *M*; on the assumption that it reacted rapidly with the solvent, the proportion of acetic acid to acetic anhydride was thus never in excess of 10 mole %. Investigation showed that the benzene nitration rate is not critically sensitive to acetic acid concentrations of this order.

To simplify the treatment of the rate data, the reaction was conducted with a large excess of nitric acid to benzene, of order at least 10:1. The rate was followed by spectrophotometric analysis for nitrobenzene in test samples diluted to appropriate concentrations in water. Using a Beckman Model DU spectrophotometer, the molar absorbancy index for nitrobenzene was found to be 7620 at 268 mμ and light absorption by other constituents of the reaction mixtures at that wave length was found to be negligible by comparison. The reaction mixtures themselves were initially quite colorless but after several hours (beyond the

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[2] John Simon Guggenheim Memorial Fellow, 1957, on leave from Harpur College, State University of New York, Endicott, New York.

[3] R. J. Gillespie and D. J. Millen, *Quart. Revs.*, **2**, 277 (1948).

[4] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 269–288.

[5] V. Gold, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2467 (1950).

[6] H. Burton and P. F. G. Praill, *ibid.*, 729 (1955).

[7] J. Chédin and S. Fénéant, *Compt. rend.*, **229**, 115 (1949).

[8] R. A. Marcus and J. M. Fresco, *J. Chem. Phys.*, **27**, 564 (1957).

[9] F. H. Cohen and J. P. Wibaut, *Rec. trav. chim.*, **54**, 409 (1935).

usual period of observation for the rate measurements) they showed a perceptible yellowish-brown color with gradual development of NO_2 fumes.

Preliminary data indicated in agreement with previous observations[9] that the rate was first order with respect to benzene. The pseudo-first-order rate coefficient k_1, however, defined by the equation

$$k_1 = \frac{1}{t - t_0} \ln \frac{b_0 - y}{b_0} \qquad (1)$$

where b_0 is the initial benzene concentration at time t_0 and y the nitrobenzene concentration at time t, drifted downward at a significant rate with increasing time. This effect is attributable to reaction of nitric acid with the solvent, ultimately yielding tetranitromethane.[9,10] Since it appeared that k_1 had a "half-life" independent of the initial nitric acid concentration, the assumption was tested that the side reaction satisfied a first-order rate law with respect to nitric acid, at least during its early stage.

Such a rate law leads to a nitric acid concentration satisfying the equation

$$a = a_0 e^{-k't} \qquad (2)$$

where a_0 is the initial concentration at time 0. Under the conditions of these experiments, with a large initial excess of nitric acid over benzene, the consumption of nitric acid by benzene is relatively negligible. Assuming then a rate law for the benzene nitration of the form

$$\frac{dy}{dt} = ka^n b \qquad (3)$$

one obtains by integration

$$-\ln \frac{b_0 - y}{b_0} = \frac{ka_0^n}{nk'} e^{-nk't_0} [1 - e^{-nk'(t-t_0)}]$$

where t_0 is the time at which the benzene is added to the nitric acid–acetic anhydride mixture. Introducing (1) defining k_1

$$k_1 = k_1^0 \frac{1 - e^{-x}}{x} \qquad (4)$$

where

$$x = nk'(t - t_0) \qquad (5)$$

and

$$k_1^0 = ka_0^n e^{-nk't_0} \qquad (6)$$

In other words, one should be able to fit the data for a given run by means of equation 4 containing two disposable parameters, nk' and k_1^0. The test for consistency is a constant value for nk' over runs with different initial nitric acid concentrations. If furthermore one allows a fixed time interval to elapse between the mixing of the nitrating mixture (t = 0) and addition of the benzene ($t = t_0$), one can find the value of the index n simply from the slope of log k_1^0 *vs.* log a_0. No commitment need be made concerning the actual species involved with benzene in the rate step.

Accordingly the following procedure was adopted. The nitrating mixture was prepared by gradual addition of a weighed quantity of nitric acid to acetic anhydride contained in a 50-ml. volumetric flask immersed in an ice-bath. The flask, calibrated both to contain and to deliver, was then immersed in an oil thermostat at 25.00° and rapidly brought almost to mark with acetic anhydride. During an ensuing time interval of 13 minutes, final adjustment of the volume was made and the contents were transferred to a small glass-stoppered erlenmeyer flask. The run was started by the addition of a measured volume (usually 5 ml.) of a standard solution of benzene in acetic anhydride. The initial benzene concentration was in the range 0.04–0.2 M. Samples were withdrawn at intervals by means of a calibrated automatic 5 ml. transfer pipet and immediately were run into distilled water contained in a 500-ml. or 1000-ml. volumetric flask. They were further diluted with water as necessary to nitrobenzene concentrations in the range 2×10^{-5} to 1×10^{-4} M, for spectrophotometric analysis. For the more rapid runs, going practically to completion within an hour or so, final readings agreed within experimental error with those predicted from the initial benzene concentrations. For the slower runs, the rate decelerated to such an extent that "final" readings could not be obtained before appreciable oxidation of the solvent had occurred.

Acetic anhydride was prepared from the B. & A. A. C. S. reagent by treatment with sodium followed by distillation under reduced pressure.[11] The untreated reagent, however, gave essentially the same results and was accordingly used for some of the runs.

Results

Figure 1, in which log k_1 is plotted against log $(t - t_0)$ for two typical runs, shows how equation 4 fits the data. The curves drawn in this figure are the theoretical function log $[(1 - e^{-x})/x]$ plotted against log x and they were fitted to the experimental points by a combination of horizontal and vertical displacements (these were actually determined by an analytical method). According to equations 4 and 5, the vertical displacement essentially determines log k_1^0 while the horizontal displacement determines $-$log nk'. Over a series of runs at initial nitric acid concentrations between 0.4 and 2 M corresponding with a thirty-fold variation in k_1^0, the derived values of nk' were reasonably constant at $(4.5 \pm 0.3) \times 10^{-4}$ sec.$^{-1}$.

In Fig. 2, log k_1^0 has been plotted against log a_0 (equation 6). One sees that n has a value slightly greater than 2; the best straight line through the experimental points in fact has a slope of 2.18.

Figure 2 includes also a set of data obtained with sulfuric acid present at 0.0100 M concentration. The values of nk' derived from the individual runs were gratifyingly independent of the initial nitric acid concentration, averaging $(6.1 \pm 0.1) \times 10^{-4}$ sec.$^{-1}$. The pronounced catalytic effect of sulfuric acid on the benzene nitration rate is evident but of even greater significance is the change in order with respect to nitric acid. Over the range investigated, k_1^0 is proportional within experimental error to the first power of the initial nitric acid concentration. Perchloric acid produced a yellow coloration when dissolved in acetic anhydride and hence its catalytic effect on the nitration rate was not investigated.

The experimental point for 0.0010 M sodium nitrate in Fig. 2 shows the marked retarding effect of this salt at 2 M nitric acid concentration. It was introduced into the reaction mixture by dissolving it in the nitric acid before the acid was combined with the acetic anhydride. Even at 0.0005 M concentration (not shown in the figure), the rate for 2 M nitric acid was depressed to about half that observed in the absence of the salt. The rate of the solvent reaction also was lowered; the value of nk' in the presence of 0.0010 M sodium nitrate was 0.92×10^{-4} sec.$^{-1}$ as compared with 4.5×10^{-4} sec.$^{-1}$ in its absence.

Because of nk' differences, the k_1^0 values for the different series of measurements shown in Fig. 2 are not strictly comparable with each other. They should be multiplied by $e^{nk't_0}$ (see equation 6) to allow for time elapsed (t_0 = 780 sec.) between compounding of the nitrating media and introduction of the benzene. While care was taken to ensure uniform treatment of the reaction mixtures so that t_0 would be approximately the same for each run, its absolute value is subject to uncertain correction for the effects of temperature equilibration and final adjustment of the concentration.

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[10] "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 803–805.

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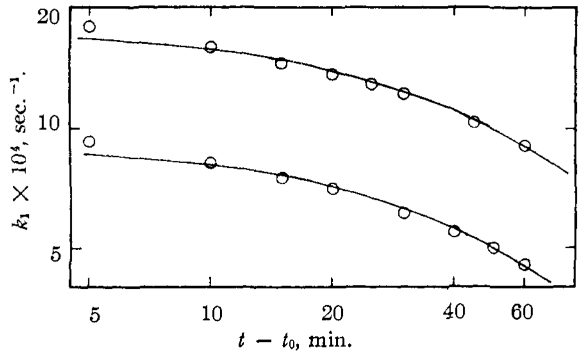


Fig. 1.—Log k_1 *vs.* log ($t - t_0$) for nitration of benzene in nitric acid–acetic anhydride solutions at 25°. Upper, 1.987 *M* HNO_3; lower, 1.521 *M* HNO_3. Solid curves are the theoretical function, log $[(1 - e^{-x})/x]$ *vs.* log x with suitable displacements of co-ordinate scales.

Several runs were carried out with solvent consisting of acetic anhydride mixed with acetic acid and the results are summarized in Table I. The proportion of acetic anhydride to acetic acid was computed on the assumption that any water introduced with the nitric acid (92% HNO_3) was entirely converted to acetic acid by reaction with the anhydride. Of greatest interest is the fact that benzene nitration in 50% acetic anhydride–acetic acid proceeds at practically the same rate as in acetic anhydride itself (containing 5–10% acetic acid). A similar result was noted by Marcus and Winkler[12] for the reaction of nitric acid with the organic nitramine, PHX; addition of as much as 26 volume % of acetic acid to the solvent acetic anhydride had no significant effect on the rate. As one should expect, however, dilution of the acetic anhydride reduces its own rate of reaction with nitric acid, as is indicated by the lower values obtained for *nk'*. The benzene nitration rate falls off with further dilution of the acetic anhydride. It is much slower but still measurable when the solvent contains 5% acetic anhydride and 95% acetic acid. A trial with 1.48 *M* nitric acid in acetic acid itself, however, yielded no detectable nitrobenzene during 8 hr. at 25°.

TABLE I

NITRATION OF BENZENE IN ACETIC ACID–ACETIC ANHYDRIDE SOLUTIONS AT 25°

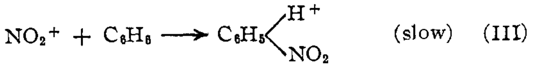
% by wt. of acetic anhydride	a_0, HNO_3, moles l.$^{-1}$	$k_1^0 \times 10^4$, sec.$^{-1}$	$nk' \times 10^4$, sec.$^{-1}$
50	1.307	5.07	1.45
50	2.014	19.0	1.45
25	1.363	2.18	0.47
5	1.335	0.32	0.10

Discussion

The results on the whole favor nitronium-ion attack on benzene as the rate-determining step

$$HNO_3 + H^+ = H_2NO_3^+ \qquad \text{(equil.)} \qquad \text{(I)}$$

$$H_2NO_3^+ + Ac_2O = NO_2^+ + 2AcOH \qquad \text{(equil.)} \qquad \text{(II)}$$



$$NO_2^+ + C_6H_6 \longrightarrow C_6H_5\langle{}^{H^+}_{NO_2} \qquad \text{(slow)} \qquad \text{(III)}$$

Such a mechanism accounts for the first-order dependence of rate on nitric acid concentration in the presence of sulfuric acid if the latter functions as a strong acid in acetic anhydride solutions and the former as a weak one. The high-order dependence on nitric acid concentration in the absence of added strong acid is then a consequence of the dual role assumed by nitric acid in itself providing the proton acquired in step I.

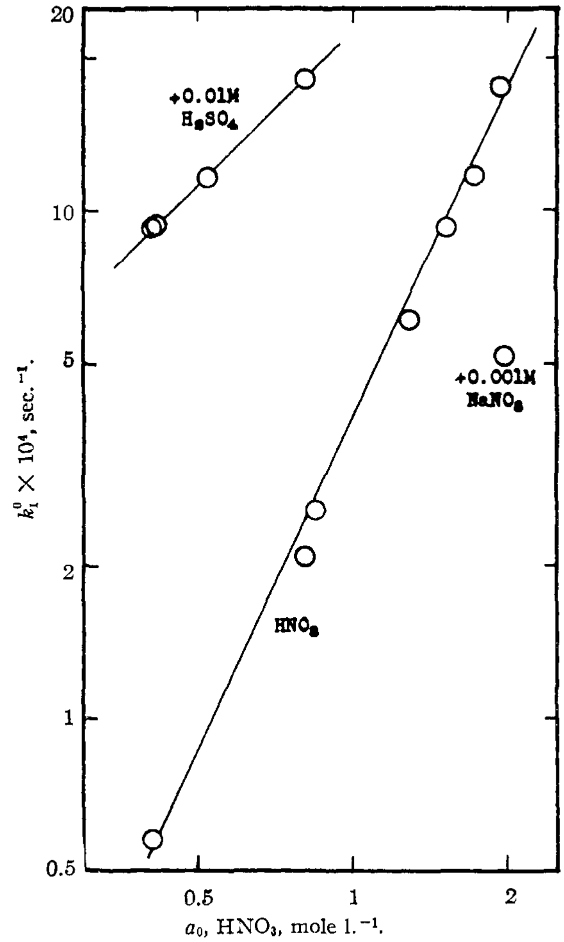


Fig. 2.—Log k_1^0 *vs.* log a_0 for nitration of benzene in nitric acid–acetic anhydride solutions at 25°.

If these were ideal solutions of electrolytes, one would expect the weak acid to provide a hydrogen ion concentration increasing in approximate proportion to the square root of the stoichiometric concentration. The above mechanism would then lead to a 1.5-order dependence of rate on nitric acid concentration. In a solvent with dielectric constant[13] 21 at 25°, however, the ionization of nitric acid probably does not satisfy the equilibrium law in its ideal form, particularly since the dielectric constant itself may well undergo change over the not inconsiderable range of nitric acid concentrations covered in the rate measurements. A second-order dependence on nitric acid concentration would be quite consistent with a mechanism in which the ion pair, $NO_2^+NO_3^-$, or even molecular N_2O_5 served as the carrier. Such a mechanism fails however to account for the retarding effect of added sodium nitrate.

The benzene nitration rates determined by Cohen and Wibaut[9] for nitric acid concentrations between 0.3 and 0.8 *M* are lower by a factor of 3 at the higher

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(12) R. A. Marcus and C. A. Winkler, *Can. J. Chem.*, **31**, 602 (1953).

(13) J. M. Tedder, *J. Chem. Soc.*, 2646 (1954).

and 5 at the lower concentrations than those reported here. They employed benzene concentrations more nearly equivalent to the nitric acid concentrations and measured "initial" rates of nitrobenzene formation over time intervals of order 30–90 minutes. The present investigation indicates that the solvent reaction could slow the benzene nitration rate considerably (the half-life for nitric acid in equation 2 is about one hour) during such a time interval. The effect furthermore would be relatively greater at the lower nitric acid concentrations than at the higher because the rate of the solvent reaction varies as the first power of the nitric acid concentration whereas the benzene nitration rate varies as a higher power. They thus reported a higher-order dependence of rate on nitric acid concentration, close to third, than that reported here.

Cohen and Wibaut measured the rate of disappearance of nitric acid in acetic anhydride with time, obtaining results considerably lower than the present experiments indicate. Their analytical procedure, however, the determination of unreacted nitrate ion by Devarda's method, may well reduce some of the combined nitrogen in the lower products of nitration, as they have pointed out. An attempt was made in the present investigation to determine nitric acid in acetic anhydride or in acetic acid by non-aqueous titration with pyridine but the end-point, indicated by glass-electrode potentiometry, is insufficiently sharp for analytical precision.

The nitric acid–acetic anhydride reaction itself is clearly not a simple one and merits further study in view of the practical importance of the system.

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Ortho–Para Directive Effects for Aromatic Nitration in Acetic Anhydride

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The nitration of chlorobenzene and of bromobenzene in nitric acid–acetic anhydride solutions containing a relatively low concentration of sulfuric acid as catalyst yields a higher proportion of the *para*-substituted product than is obtained by nitration with aqueous 90% nitric acid. This effect is opposite to that observed with anisole and other compounds previously studied, where nitration in acetic anhydride yields a higher proportion of the *ortho*-substituted isomer. The results are consistent with a nitronium ion mechanism for both media on the supposition that in the medium of lower dielectric constant, electrostatic interaction between ion and dipole plays a significant role.

Existing data for the nitration of aromatic compounds containing an *ortho–para* directing group suggest that if one uses acetic anhydride as solvent in place of water, there is an increase in the proportion of *ortho*-substituted to *para*-substituted product. The effect is well established for the nitration of anisole,[2,3] acetanilide[4,5] and propionanilide[5] but there is practically no effect in the case of toluene.[6] For anisole, an attempt has been made recently to account for the "*ortho* effect" on steric grounds.[3] If the nitrating agent in acetic anhydride is a molecular compound such as acetyl nitrate, one can envision a mechanism whereby the directing group assists the incoming molecule, thus favoring substitution at the *ortho* position. The absence of a hydrogen-isotope effect in this position,[3] however, shows that displacement of the proton is not involved in the rate-determining transition state. If on the other hand the actual mechanism is electrophilic addition of nitronium ion,[7,8] as in aqueous solutions, then a different explanation is suggested, based on the polar character of the directing group and the dielectric constant of the solvent.

Because of the inhomogeneous nature of the intervening medium,[9] it is difficult to estimate the electrostatic free energy between the attacking positively charged ion and the dipole moment associated with the *ortho–para* directing substituent. Qualitatively, however, one would expect that for a dipole with its positive end directed outward from the ring, as in the cases of the methoxy and the anilide groups, electrostatic interaction would favor the nearer *ortho* position relatively to the more distant *para* and that this effect might be enhanced to some extent in a solvent of lower dielectric constant. One does not have to suppose that the polar effect is predominant but only that it will be superimposed on other factors determining the actual rates of reaction at the respective sites. On the basis of this argument, the small effect of the solvent in the case of toluene nitration could be associated with the comparatively small dipole moment contributed by the methyl group itself.

It would follow that for substituents providing dipole moments with the negative end directed outward from the ring, such as the chloro and bromo groups, *ortho* substitution should be suppressed relatively to *para* in acetic anhydride as compared with water. The present investigation shows that this is the case. When chlorobenzene is nitrated at 0° in acetic anhydride containing 2 M HNO_3 with 0.04 M H_2SO_4 present as acid catalyst,[8] the proportion of *o*- to *p*-chloronitrobenzene in the product is 10–90 as compared with 30–70 obtained by nitration with

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[1] John Simon Guggenheim Memorial Fellow, 1957, on leave from Harpur College, State University of New York, Endicott, New York.

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[9] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938); *Trans. Faraday Soc.*, **43**, 77 (1947).