194. *The Prototropy of the Nitromethanes. Part I. Chloro-, Bromo-, and Nitro-phenylnitromethanes.*

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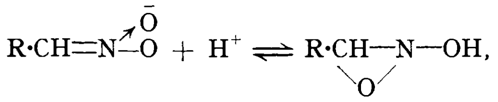
The rate of prototropic change from the *iso*nitro-ion to the normal nitro-form has been followed in aqueous ethanol (50%) solutions of *o*-, *m*-, and *p*-chloro-, -bromo-, and -nitro-phenylnitromethanes. The order observed is $NO_2 > Hal. > H$, so the change is a Class B reaction according to Ingold and Rothstein's classification.

The curves generally are of a two-fold type, first showing a concavity upwards, but later a linear relationship such as has previously been observed by Branch and Jaxon-Deelman with nitromethane and phenylnitromethane. A similar mechanism may therefore be assumed in all the cases examined. *o*-Nitrophenylnitromethane gives an abnormal curve.

The velocity of prototropic change is in the sense (*o*), $p > m$ for the nitro-compounds, but the halogeno-compounds do not show such an effect.

It was shown by Hantzsch (*Ber.*, 1896, **29**, 2251; 1899, **32**, 607) that the reversible electrolytic dissociations of nitromethanes are sufficiently slow in both directions to allow the change in electrical conductivity to be measured when their salts are formed by reaction with bases or when such salts react with hydrogen ions. The slow rates of these ionic reactions are attributed to structural change, and Branch and Jaxon-Deelman (*J. Amer. Chem. Soc.*, 1927, **49**, 1765; see also Ingold, *Ann. Reports*, 1927, **24**, 107) carried out more exact conductometric measurements with nitromethane and phenylnitromethane in order to measure the rates of reaction and elucidate the mechanism of the change. They concluded that the two-fold character of the curves they obtained could be explained by assuming the formation of a second type of *iso*nitro-compound by a reversible reaction, such as



$$R{\cdot}CH{=}N\overset{\bar{O}}{\nearrow}{-}O + H^{+} \rightleftharpoons \underset{\diagdown O \diagup}{R{\cdot}CH{-}N{-}OH},$$

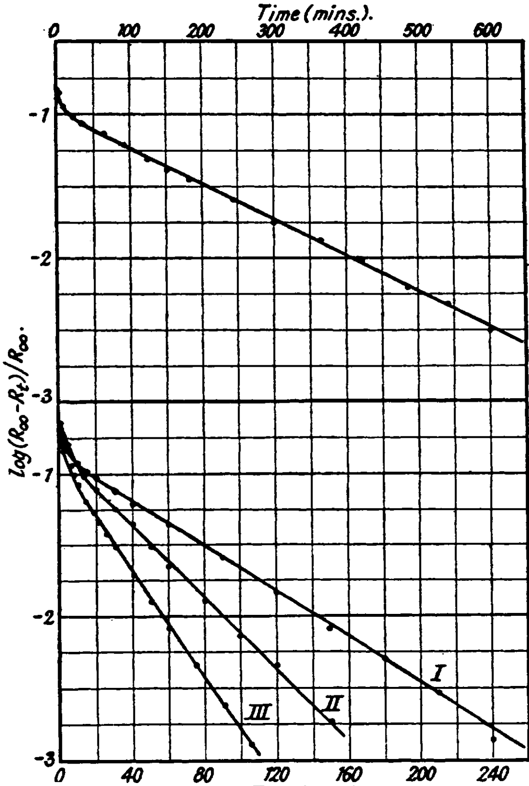
which is followed by a comparatively slow change of the ion of the *iso*nitro-acid to an ion which combines rapidly with a hydrogen ion to form the normal un-ionised nitro-compound, the reaction being unimolecular. Their formulations, however, require some modification in view of the later work of Kuhn and Albrecht (*Ber.*, 1927, **60**, 1297) and Shriner and Young (*J. Amer. Chem. Soc.*, 1930, **52**, 3332) on the optical activity of certain *iso*nitromethane salts.

The object of the present investigation was to determine the effect, if any, of substituents in the benzene nucleus on the rate of prototropic change of phenylnitromethanes; and to see from the graphical results if a similar mechanism to that advanced by Branch and Jaxon-Deelman (*loc. cit.*) was valid. Whatever the actual course of the change from the *iso*nitromethane to the normal form, a recession of electrons from the end of the side chain towards the nucleus, with the consequent concentration of charge on the " methane " carbon atom, may be expected to promote the change. Hence, the presence of groups such as nitroxyl or of atoms with high electron affinities, such as the halogens, should increase the rate of prototropic change; whereas substituents of opposite electrical character should exert a deactivating effect. Substitution effects on this type of unsymmetrical triad mobility have not been studied to any great extent, and the conditions under which the reaction has been examined are unusual in work on side-chain reactivity: the low temperature, low concentration, and absence of excess of mineral acid or alkali should reduce disturbing effects to a minimum.

The rates of reaction were measured only in one direction, *viz.*, that of the formation of the nitro-compounds by the combination of ions; and under the experimental conditions secondary decomposition of the nitro-compounds may be regarded as negligible.

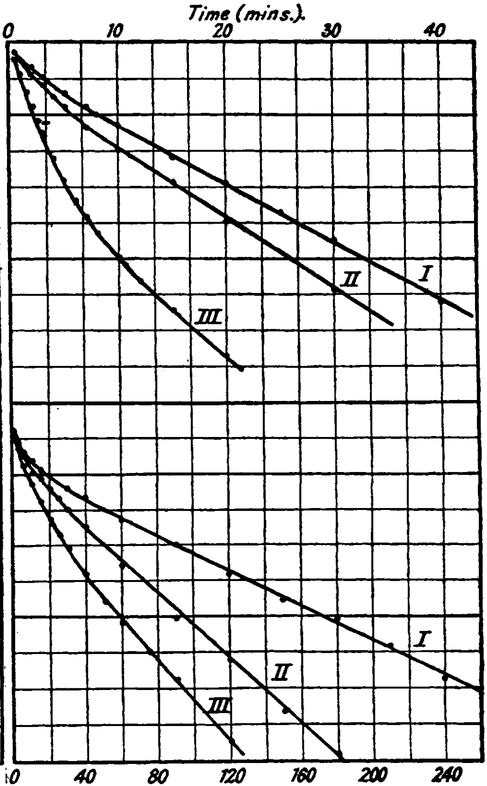
The experimental curves are shown in Figs. 1 and 2, in which $\log (R_\infty - R_t)/R_\infty$ is plotted against time, R_t being the resistance at time t, and R_∞ that after all significant change has ceased. With one exception these display the two-fold character described by Branch and Jaxon-Deelman, being concave upwards at the outset but later assuming a linear form. Similar mechanisms may therefore be postulated in all the cases so far examined.

FIG. 1.



Upper curve : Phenylnitromethane.
Lower curves : (I) p-, (II) m-, (III) o-*Bromophenylnitromethane.*

FIG. 2.



Upper curves : (I) m-, (II) p-, (III) o-*Nitrophenylnitromethane.*
Lower curves : (I) p-, (II) m-, (III) o-*Chlorophenylnitromethane.*

The rates of prototropic change obtained from the linear portion of each curve are set out below, that of the parent phenylnitromethane being taken as unity.

Substituent.	*o*-.	*m*-.	*p*-.
NO_2	*	16·40	19·60
Br	7·50	5·00	3·23
Cl	5·73	4·5	2·51

* Abnormal.

Ingold and Rothstein (J., 1928, 1217) have grouped side-chain reactions in two classes, A and B, in which the change is facilitated respectively by accession of electrons to, and by recession of electrons from, the point of attack. Qualitatively it has been shown that a substituent which accelerates reactions of one class frequently retards those of the other; *e.g.*, the order $CH_3 > H > \text{Halogen} > NO_2$ holds throughout Class A, and the reverse order throughout Class B. From the results recorded above it is evident that the prototropy of the phenylnitromethanes is a Class B reaction, and the qualitative relationship in so far as it has been examined holds good.

A summary of work on side-chain reactions (Williams, J., 1930, 40) shows that with few exceptions the accelerating effect of nitroxyl is in the sense $o, p > m$. In agreement with this, we find that the rate of prototropic change in the case of the *p*- exceeds that of the *m*-compound; but it is not possible to submit data for the *o*-derivative, as this curve is the only exceptional one recorded.

The concavity upwards in this curve in the region in which linear relationships are found in all other cases may be due to some "ortho-effect" of the nitro-group (cf. Williams, *loc. cit.*; van Duin, *Rec. Trav. chim.*, 1927, **46**, 256; Kindler, *Annalen*, 1928, **464**, 278; Baddeley and Bennett, J., 1933, 263). An analogous effect has not been observed in the case of the chloro- or bromo-compounds.

EXPERIMENTAL.

Measurements.—The reaction was followed conductometrically by Branch and Jaxon-Deelman's procedure (*loc. cit.*). The temperature in each case was 0°, and the solvent aqueous ethanol (500 c.c. of ethanol per l.). Equal volumes of 0·01M-solutions of hydrochloric acid and the nitromethane sodium salt were mixed, giving a final concentration of 0·005M with respect to both the *ψ*-acid and the sodium chloride. For each substance several separate determinations were carried out, the curves being drawn from the mean values. The mean velocity constants given by the slope of the curves lead to the following values of *k* :

Substituent.	10^4k (sec.$^{-1}$).	Substituent.	10^4k (sec.$^{-1}$).	Substituent.	10^4k (sec.$^{-1}$).
(Unsubstituted) ...	0·94	*o*-Chloro-	5·38	*o*-Bromo-............	7·05
m-Nitro-	15·4	*m*- „	4·23	*m*- „	4·70
p- „	18·4	*p*- „	2·36	*p*- „	3·03

Materials.—The aryl nitromethanes were prepared by one or other of two general methods.

Method (a). The corresponding benzyl iodide is shaken for some hours in ethereal solution with a slight excess of freshly prepared silver nitrite, and the mixture kept overnight. Silver iodide is filtered off, and 5% sodium methoxide added to the filtrate. The precipitated nitromethane sodium salt is washed with ether, dissolved in water, and acidified with hydrochloric acid, the liberated nitromethane being worked up in the usual way. The following compounds were thus prepared, and crystallised from ethanol unless otherwise specified : *o*-Nitrophenylnitromethane, pale yellow needles, m. p. 71—72° (Holleman, *Rec. Trav. chim.*, 1896, **15**, 367); *m*-isomer, yellow needles, m. p. 94—95° (Hantzsch, *Ber.*, 1907, **40**, 1555); *p*-isomer, yellow needles, m. p. 91—92° (Hantzsch and Veit, *Ber.*, 1899, **32**, 621); *p*-chlorophenylnitromethane, colourless needles, m. p. 33° (van Raalte, *Rec. Trav. chim.*, 1899, **18**, 392); *p*-bromophenylnitromethane, colourless needles from light petroleum, m. p. 58° (Wislicenus and Elvert, *Ber.*, 1908, **41**, 4129).

Method (b). Equimolecular proportions of the substituted phenylacetonitrile, ethyl nitrate, and potassium ethoxide are allowed to condense in alcoholic solution at room temperature. The deep brown-red solution soon deposits crystals of the potassium salt of the *iso*nitroacetonitrile (potassium gives better yields than sodium in this reaction). The precipitation is completed by addition of ether, and after being collected and washed with ether, the solid is hydrolysed by boiling with 20% sodium hydroxide solution until ammonia is no longer evolved. After concentration until crystals begin to separate, the liquid is cooled, and the solid sucked dry. The mass is dissolved in water and the nitromethane liberated by acidification of the ice-cold solution is worked up in the usual way. The following compounds were thus prepared : Phenylnitromethane, b. p. 105°/13 mm. (Wislicenus and Endres, *Ber.*, 1902, **35**, 1759); *o-chlorophenylnitromethane*, yellow oil, b. p. 109°/10 mm. (Found : N, 8·4. $C_7H_6O_2NCl$ requires N, 8·2%); *m-chlorophenylnitromethane*, yellow oil, b. p. 128°/13 mm., solidifying on cooling to a mass of crystals, m. p. 23° (Found : C, 49·4; H, 3·7; N, 8·2. $C_7H_6O_2NCl$ requires C, 49·0; H, 3·5; N, 8·2%); *o*-bromophenylnitromethane, yellow oil, b. p. 139°/7 mm. (Found : Br, 37·2. Calc. for $C_7H_6O_2NBr$: Br, 37·1%) (Wislicenus and Fischer, *Ber.*, 1910, **43**, 2238, report white crystals, m. p. 55—56°); *m-bromophenylnitromethane*, long white needles, m. p. 23—24°, from light petroleum at low temperatures (Found : C, 39·5; H, 2·75. $C_7H_6O_2NBr$ requires C, 38·9; H, 2·8%).

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