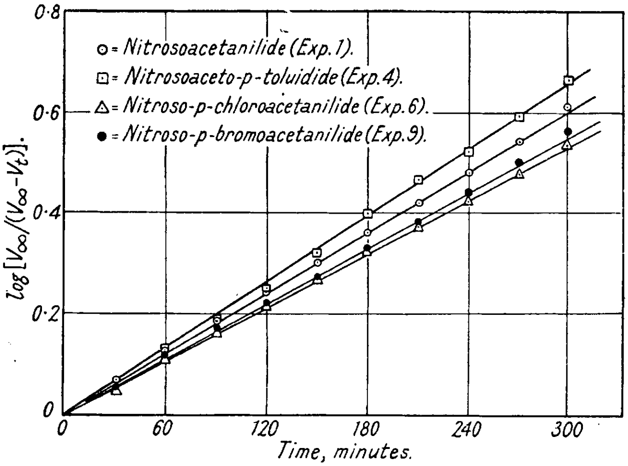
153. *The Rate of Decomposition of Some* p-*Substituted Nitrosoacetanilides in Benzene.*

By WILLIAM S. M. GRIEVE and DONALD H. HEY.

THE rate of decomposition of benzenediazonium salts and its relationship to the presence and position of substituent groups in the aromatic nucleus have attracted the attention of many workers (Hirsch, *Ber.*, 1891, **24**, 324; Hausser and Muller, *Compt. rend.*, 1892, **114**, 549, 669, 760, 1438; Oddo, *Gazzetta*, 1895, **25**, 327; Oddo and Ampola, *ibid.*, 1896, **26**, 541; Hantzsch, *Ber.*, 1900, **33**, 2517; Hantzsch and Thompson, *Ber.*, 1908, **41**, 3519; Euler, *Annalen*, 1902, **325**, 292; Cain and Nicoll, J., 1902, **81**, 1412; 1903, **83**, 206, 470; Yamamoto, *J. Soc. Chem. Ind. Japan*, 1929, **32**, 279, 308, 352; 1930, **33**, 177, 231, 358; 1932, **35**, 11, 298, 564; 1933, **36**, 59, 490, 609; 1934, **37**, 29, 400, 512; Snow, *Ind. Eng. Chem.*, 1932, **24**, 1420). From the results of these investigations, it is possible to construct a series in order of stability, and, with reference to the following substituent groups in the aromatic nucleus, the order of decreasing stability is : *p*-OMe, *p*-Cl, *p*-Br, *p*-Me, H, *m*-Me. The most striking feature of these results is the magnitude of the differences in stability which they reveal. These differences are sufficiently large to render impracticable the measurement of the velocities of decomposition for the complete series at any one temperature, but by extrapolation the following comparative figures can be obtained (based on Euler's measurements), the velocity constant for *p*-methoxybenzenediazonium chloride, the most stable member of the series selected, being taken as unity : *p*-OMe 1, *p*-Cl 12·5, *p*-Br 22·5, *p*-Me 149·5, H 2241, *m*-Me 6640.

On the other hand, little attention has been paid to the rates of decomposition of the sodium diazoate of benzene and substituted benzenes, but recent observations by Blumberger (*Rec. trav. chim.*, 1930, **49**, 276), Jolles (*Atti R. Accad. Lincei*, 1932, **15**, 292, 395), and Oddo and Indovina (*Gazzetta*, 1932, **62**, 1119, 1138) have shown that the decomposition in alkaline solution is of a more complicated nature. Nevertheless, Jolles and Camiglieri (*ibid.*, p. 720) investigated the rates of decomposition of sodium benzenediazoate and a somewhat limited series of substituted benzenediazoates, and found that the order of stability was the reverse of that which obtains in the diazonium salt series. No velocity constants were calculated, but the following decreasing order of stability was revealed : *m*-Me, H, *p*-Me, *p*-OMe. Although the reversal in the order of stability is complete, the exact significance of these measurements is somewhat obscure, owing to their dependence on the alkalinity of the medium (cf. Blumberger, *loc. cit.*; Oddo and Indovina, *loc. cit.*) and to the possibility of the transformation of the normal (*syn*)-diazoates into the more stable *iso*(*anti*)-diazoates.



Velocity measurements have now been made for the decomposition of nitrosoacetanilide and a series of substituted nitrosoacetanilides, which may be in tautomeric equilibrium with the acetyl derivatives of the corresponding diazoates : $\mathrm{Ar{\cdot}N(NO){\cdot}CO{\cdot}CH_3 \rightleftharpoons Ar{\cdot}N{:}N{\cdot}O{\cdot}CO{\cdot}CH_3}$. The velocity of decomposition of nitrosoacetanilide itself in a series of solvents has already been measured, and the reaction found to be unimolecular or quasi-unimolecular (Grieve and Hey, J., 1934, 1797). The number of substituted nitrosoacetanilides available for study is confined to those prepared from *p*-toluidine and *p*-bromo- and *p*-chloro-aniline. Since attempts to prepare other nitrosoacetanilides were unsuccessful (see p. 691), direct comparison with the results of Jolles and Camiglieri on the sodium diazoates cannot be made.

Quantitative measurements of the rate of decomposition of the nitroso-derivatives of acetanilide, aceto-*p*-toluidide, and *p*-chloro- and *p*-bromo-acetanilide in benzene were carried out by observing the rate of evolution of nitrogen. In each case, good unimolecular velocity constants were obtained, all of which, however, fall within a small range, as shown in the accompanying diagram, which represents the course of the reactions up to 75—80% of completion. In the four examples studied, the order of decreasing stability is *p*-Cl, *p*-Br, H, *p*-Me. These results are in marked contrast to the much larger differences observed between the velocity constants for the decomposition of the corresponding diazonium salts.

EXPERIMENTAL.

Nitrosoacetanilide (m. p. 50—51°) was prepared by passing nitrous fumes into a solution of acetanilide in glacial acetic acid and precipitating the product with water (Grieve and Hey, *loc. cit.*). Nitrosoaceto-*p*-toluidide, m. p. 80° (Fischer, *Ber.*, 1877, **10**, 959; Kliegl and Huber, *Ber.*, 1920, **53**, 1655), nitroso-*p*-chloroacetanilide, m. p. 83—84° (Bamberger, *Ber.*, 1897, **30**, 368; Bamberger and Baudisch, *Ber.*, 1909, **42**, 3589), and nitroso-*p*-bromoacetanilide, m. p. 88° (Bamberger, *loc. cit.*; Bamberger and Baudisch, *loc. cit.*; Hantzsch and Wechsler, *Annalen*, 1902, **325**, 242) were prepared in similar manner.

The measurements of the rate of evolution of nitrogen for solutions of the four nitrosoacetanilides in pure thiophen-free benzene, previously saturated with nitrogen, were carried out at 20° in the apparatus previously described (Grieve and Hey, *loc. cit.*). The quantity of the nitroso-compound dissolved in 100 c.c. of benzene was equivalent to 2·000 g. of nitrosoacetanilide in order that the total nitrogen content might be the same in each case. About 20—30 c.c. of nitrogen were allowed to escape before half-hourly readings were taken over a period of 6—7 hours, and the final volume of nitrogen was read after the lapse of at least 24 hours. The volumes of gas evolved were corrected, and the results obtained by plotting $\log [V_\infty/(V_\infty - V_t)]$ against t, where V_∞ is the final observed volume and V_t the volume at time t, are shown in the diagram. The total volumes of nitrogen liberated from the different nitrosoacetanilides, which vary from about 75 to 90%, for nitrosoaceto-*p*-toluidide and nitrosoacetanilide respectively, together with the unimolecular velocity constants, given by the equation $k = 2{\cdot}303/t.\ \log V_\infty/(V_\infty - V_t)$, are shown in the following table:

	Nitrosoacetanilide in 100 c.c. benzene.	Wt. of solute, g.	Vol. of N_2 evolved, c.c.	N_2 evolved, %.	$k.10^3$.
1.	Unsubstituted	2·0000	248·0	90·8	4·61
2.	,, ...	2·0000	247·8	90·7	4·59
3.	,, ...	2·0000	240·5	88·0	4·53
4.	*p*-Methyl	2·1707	206·2	75·5	5·02
5.	,, ...	2·1707	203·7	74·6	4·96
6.	*p*-Chloro	2·4209	240·7	88·1	4·09
7.	,, ...	2·4209	241·5	88·4	4·15
8.	,, ...	2·4209	243·1	89·0	4·08
9.	*p*-Bromo-	2·9634	216·5	79·3	4·24
10.	,, ...	2·9634	224·2	82·1	4·22

Attempts to prepare the nitroso-derivatives of other acetylated bases by the method outlined above were unsuccessful. In the case of *p*-nitroacetanilide the dark green solution, obtained on passing nitrous fumes into a solution of the anilide in glacial acetic acid, evolved oxides of nitrogen when poured into water and *p*-nitroacetanilide was precipitated. With aceto-*m*-toluidide a yellow oil separated when the reaction mixture was poured into water, but before separation could be effected nitrogen was freely evolved with the formation of a black tar. With the acetyl derivatives of *o*-chloroaniline, *p*-anisidine, and α- and β-naphthylamine, dark oily products were precipitated, from which nitrogen was freely evolved. The yellow oil, which separated when the reaction mixture from aceto-*p*-phenetidide was poured into water, was extracted with ether, on evaporation of which yellow needles separated. There was no evolution of nitrogen. Recrystallisation from water or dilute alcohol gave 3-nitro-4-acetamidophenetole, m. p. 103° (Wender, *Gazzetta*, 1889, **19**, 219), which was identified by hydrolysis with concentrated hydrochloric acid to 3-nitro-4-aminophenetole, red prisms, m. p. 112° (cf. Wender, *loc. cit.*), and by nitration with fuming nitric acid at 0—5° to 2 : 3-dinitro-4-acetamidophenetole, yellow needles, m. p. 206° (cf. Wender, *loc. cit.*; Blanksma, *Rec. trav. chim.*, 1908, **27**, 49).

THE UNIVERSITY, MANCHESTER.

[*Received, April* 5*th*, 1935.]