26. *Nitrosoacylarylamines. Part I. The Decomposition of Nitrosoacetanilide in Solution.*

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In continuation of previous work on similar lines (Grieve and Hey, J., 1934, 1798; 1935, 689) a quantitative study is made of the decomposition of nitrosoacetanilide in solution by measurement of the rate of evolution of nitrogen. Attention is directed to the influence of concentration and of temperature on the reaction in benzene solution, and also to the reaction in a variety of solvents. The energy of activation for the reaction in benzene solution is found to be of the order of 22,000 cals. The results are in agreement with the representation of the primary reaction as a non-ionic decomposition into free radicals and molecular nitrogen.

Bamberger (*Ber.*, 1897, **30**, 366) showed that, when nitrosoacetanilide is dissolved in benzene, diphenyl is formed with liberation of nitrogen: $\mathrm{Ph{\cdot}N(NO){\cdot}CO{\cdot}CH_3 + C_6H_6 \longrightarrow Ph{\cdot}Ph + N_2 + CH_3{\cdot}CO_2H}$. Similar reactions have been carried out with nitroso-*p*-bromoacetanilide (Hantzsch and Wechsler, *Annalen*, 1902, **325**, 242), and with nitrosoaceto-*p*-toluidide (Kliegl and Huber, *Ber.*, 1920, **53**, 1655), but, apart from these instances, the reaction had received scant attention. Grieve and Hey (J., 1934, 1798) carried out a series of reactions between nitrosoacetanilide and various aromatic liquids and showed the close relationship between these reactions and those of the aryl diazoates, previously studied by Gomberg and his co-workers (*J. Amer. Chem. Soc.*, 1924, **46**, 2339; 1926, **48**, 1372), which may be represented thus: $\mathrm{Ph{\cdot}N_2{\cdot}OH + C_6H_6 \longrightarrow Ph{\cdot}Ph + N_2 + H_2O}$. In particular it was shown that in both reactions the normal rules of aromatic substitution do not hold and that reaction invariably proceeds at the aromatic nucleus at the ortho- and/or para-position with respect to any group which may be present. For this and other reasons (see Grieve and Hey, *loc. cit.*; Hey, J., 1934, 1966) it was suggested that these reactions were non-ionic in type and took place through the formation and transient existence of free radicals. More recently attention has been given to the reactions of nitrosoacetanilide by Waters (J., 1937, 112), who showed (*a*) that in many solvents nitrosoacetanilide decomposes with evolution of carbon dioxide as well as nitrogen, and (*b*) that metallic elements may be attacked during the reaction, even in the presence of an excess of calcium carbonate. These results supply strong confirmatory evidence in support of a free-radical mechanism, on the basis of which the decomposition of nitrosoacetanilide should now be more correctly represented thus:

$$\mathrm{Ph{\cdot}N(NO){\cdot}CO{\cdot}CH_3 \longrightarrow Ph{\cdot} + N_2 + CH_3CO{\cdot}O{\cdot}} \qquad \mathrm{CH_3{\cdot}CO{\cdot}O{\cdot} \longrightarrow CH_3{\cdot} + CO_2}$$

The reactions of nitrosoacetanilide in organic solvents usually take place at a conveniently measurable speed at about room temperature and quantitative studies have been carried out on the rate of evolution of nitrogen * (Grieve and Hey, *loc. cit.*). With all the solvents employed, the reaction was unimolecular in type and the velocity constants were all of the same order, thus supporting a mechanism of primary dissociation into free radicals and molecular nitrogen. The quantitative study of the reaction is now extended to include (*a*) an examination of the influence of concentration and temperature with benzene as solvent, and (*b*) the use of other solvents.

Influence of Concentration.—In order to ascertain the influence of concentration on the decomposition of nitrosoacetanilide in benzene solution experiments were carried out at 20°, in groups of three with the same sample of nitrosoacetanilide, and concentrations were varied from 2 g. to 20 g. of nitrosoacetanilide in 100 c.c. of benzene. The apparatus and the experimental procedure have been described previously (Grieve and Hey, *loc. cit.*, p. 1805). In all these and subsequent experiments, which were carried out in duplicate or triplicate, the benzene was saturated with nitrogen before use and all volumes recorded are corrected. The rate of evolution of nitrogen was observed during about six hours and the final volume of nitrogen was measured after the lapse of at least 24 hours. The yield of diphenyl formed was determined in each case. It was found that, as the concentration of nitrosoacetanilide increased, there was a corresponding increase in the total volume of nitrogen evolved, but the yield of diphenyl isolated showed a progressive decrease. This is clearly due to the formation of ter- and poly-phenyls in increasing quantity. The formation of these hydrocarbons of higher molecular weight is known to be a characteristic of these reactions (Grieve and Hey, *loc. cit.*; see also Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2341; Gerngross and Dunkel, *Ber.*, 1924, **57**, 739), and in more concentrated solution the tendency for their formation would be greater. The results of these experiments are in Table I. The small departures from an exact linear relationship must be attributed in part to slight differences in the purity of the nitrosoacetanilide used in different sets of experiments. Reference has been made previously to the difficulty of preparing uniformly pure nitrosoacetanilide (Grieve and Hey, *loc. cit.*), the purity of which may vary from about 95 to 99%. In addition, at the higher concentrations difficulty was experienced in keeping the temperature uniformly constant at 20° owing to excessive evolution of heat during the reactions.

TABLE I.

Nitroso-acetanilide, g., in 100 c.c. C_6H_6.	N_2 evolved, c.c.	N_2 evolved, %.	Ph·Ph isolated, g.	Yield of Ph·Ph, %.
2	248·0	90·8	1·5	80
2	253·8	92·7	1·5	80
3	371·6	90·4	2·0	71
5	584·7	85·3	3·6	76
5	575·9	84·1	—	—
7·5	908·3	88·4	4·7	67
9	1114·0	90·3	5·5	65
10	1200·0	87·6	5·85	62
12·5	1544·5	90·2	6·8	58
20	2352·5	85·9	8·75	46

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* The discovery by Waters (*loc. cit.*) of the concomitant evolution of carbon dioxide during the reactions of nitrosoacetanilide does not affect the results of the experiments described by Grieve and Hey (*loc. cit.*; J., 1935, 689), in which nitrometers filled with 40% aqueous potassium hydroxide were used.

It has been previously stated (Grieve and Hey, *loc. cit.*) that, although when 2 g. of nitrosoacetanilide were dissolved in 100 c.c. of benzene about 90% of the nitrogen was evolved and diphenyl could be isolated in good yield, yet when the reaction was carried out on a larger scale it was difficult to avoid the formation of tarry by-products with a consequent considerable reduction in the yield of diphenyl. In an attempt to discover the cause of this discrepancy small- and large-scale experiments were carried out side by side and it is now found that, when special precautions are taken to ensure that, as far as possible, both reactions take place under identical experimental conditions, the same percentage volume of nitrogen is evolved and the yield of diphenyl in the large-scale experiment is only slightly inferior to that in the small-scale experiment. The results obtained in one such set of experiments are in Table II.

TABLE II.

Nitrosoacetanilide, g.	C_6H_6, c.c.	N_2 evolved, c.c.	N_2 evolved, %.	Ph·Ph, g.	Yield of Ph·Ph, %.
2	100	221	81	1·5	80
20	1000	2220	81	13·5	71

Influence of Temperature.—The effect of temperature on the rate of decomposition of nitrosoacetanilide in benzene solution was studied by observing the rate of evolution of nitrogen from 2 g. of nitrosoacetanilide in 100 c.c. of benzene at four different temperatures. The results obtained are in Table III, in which the figures represent the mean values of measurements carried out in triplicate.

TABLE III.

Temp.	10°	20°	30°	40°
N_2 evolved, c.c.	239·0	249·0	238·7	257·9
k	0·00148	0·00459	0·0170	0·0595
Ph·Ph, g.	1·0	1·5	1·35	1·3
Yield of Ph·Ph, %	53	80	71	68

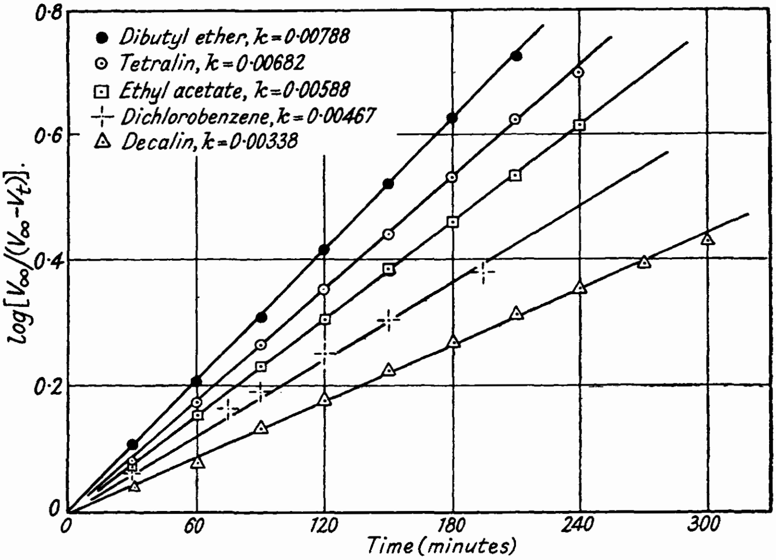
The rate of evolution of nitrogen, as expressed in the velocity constant k, increases fairly rapidly with increase in temperature, the total volume of nitrogen evolved is not appreciably affected, and the best yields of diphenyl are obtained at 20°. The energy of activation of the reaction, derived from the Arrhenius equation by plotting log k against the reciprocal of the temperature, where $\log k = -1/2{\cdot}303 \times E/\boldsymbol{R}T + c$, is found to be of the order of 22,000 cals.

Influence of Solvent.—Grieve and Hey (*loc. cit.*) showed that the rates of evolution of nitrogen from solutions of nitrosoacetanilide in carbon tetrachloride, chlorobenzene, and the other aromatic liquids employed differed but little. It was contended that this observation was not fortuitous, but was a direct result of a non-ionic fission into free radicals as the primary process in the reaction. The rates of evolution of nitrogen from solutions of nitrosoacetanilide in chloroform, trichloroethylene, tetrachloroethane, dichlorobenzene (technical), tetralin, decalin, dibutyl ether, ethyl acetate, and diethyl-*o*-toluidine have now been measured at 20° with 2 g. of solute in 100 c.c. of solvent. In each case attention was given to (*a*) the rate of evolution of nitrogen, (*b*) the total volume of nitrogen evolved, and (*c*) the identification of any products formed. In most cases there was evidence of reaction with the solvent, but, owing to the comparatively small amount of nitrosoacetanilide used, the chemical identification of the products was not always possible. The quantitative results obtained are in Table IV, in which the figures represent mean values from experiments in duplicate or triplicate. The value with benzene as solvent is included for comparison.

TABLE IV.

Solvent.	N_2 evolved, c.c.	k.	Solvent.	N_2 evolved, c.c.	k.
Benzene	253·8	0·00456	Tetralin	168·0	0·00678
Chloroform	223·0	—	Decalin	184·3	0·00332
Carbon tetrachloride	134·2	0·00416	Dibutyl ether	169·5	0·00790
Trichloroethylene	53·3	—	Ethyl acetate	173·0	0·00583
Tetrachloroethane	156·9	—	Diethyl-*o*-toluidine	8·9	—
Dichlorobenzene	205·7	0·00468			

With this range of solvents the total volume of nitrogen evolved varies within wide limits, thus showing the incidence of reactions between solvent and solute which do not involve the elimination of nitrogen. This is particularly marked in the case of diethyl-*o*-toluidine. In those cases, however, where a reliable estimation of the rate of evolution of nitrogen could be made, it was again shown that the measured reaction was unimolecular in type and that the velocity constants all fell within a narrow range and were thus not appreciably influenced by the nature of the solvent. The results of individual experiments are represented in the figure, in which log $[V_\infty/(V_\infty - V_t)]$ is plotted against t, where V_∞ is the final observed volume, and Vt the volume at time t. These observations are in agreement with the results and deductions previously obtained in support of a non-ionic fission into free radicals and molecular nitrogen. In the reactions with carbon tetrachloride and trichloroethylene some benzenediazonium chloride was precipitated from solution; with ethyl acetate, some acetaldehyde was formed.



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