(733 mm.)]. The infrared spectrum differed markedly from that of 3-butene-1-ol. For example, whereas the latter compound had a strong hand at 6.1 μ, due probably to the isolated carbon–carbon double bond, the present material had only a very small band in this region. The present material also lacked bands at 8.45, 9.5, 10.1 and 11.4 μ. Additional bands at 7.5, 8.1, 8.9, 9.1, 9.7 and 10.4 μ were present. The infrared spectrum also differed markedly from that of cyclopropylmethanol. For example, the present material did not have bands at 12.9, 12.4, 11.95 and 11.0 μ. The infrared spectrum compared favorably with that reported in the literature for cyclobutanol.[14]

The phenylurethan derivative of VII was prepared as described above for labeled cyclopropylmethanol (V) by allowing 1.32 g. (0.011 mole) of phenyl isocyanate to react with 0.74 g. (0.010 mole) of VII. After it was recrystallized five times from hexane, the phenylurethan had m.p. 131.5–132.5° (capillary) (lit.[14] 130.6–131.2°).

Anal. Calcd. for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.38; H, 7.08; N, 7.19.

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[14] J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Reactions of Diazonium Salts with Nucleophiles. V. The Substitution of Halogen by Thiocyanate[1]

BY EDWARD S. LEWIS AND HARALD SUHR

RECEIVED JUNE 4, 1959

Rates are reported for the reactions of various *o*- and *p*-halogen substituted benzenediazonium ions with thiocyanate, resulting in the substitution of thiocyanate for the halogen. Solvent effects are studied. Although the order of reactivities of *p*-halogen derivatives is *p*-I > *p*-Br > *p*-Cl > *p*-F, it is concluded that the reaction is a normal nucleophilic substitution powerfully activated by the diazonium ion group.

Introduction

Substitution of groups *ortho* and *para* to the diazonium group has long been known; among the earliest examples was that of Hantzsch and Hirsch[2] who found that when *p*-chlorobenzenediazonium thiocyanate was dissolved in alcohol and precipitated with ether, the solid product was *p*-thiocyanatobenzenediazonium chloride. Subsequent investigations by Hirsch[3] established the generality of the reaction, and Hantzsch and his co-workers[4] found that chloride ion would substitute for nuclear bromine *ortho* or *para* to the diazonium group.[4] They found in one case first-order kinetics, which now appears improbable, and also found that the rate was strongly solvent dependent. A large variety of analogous reactions is summarized by Saunders[5] showing that many groups can be lost in such reactions, in most cases from the position *ortho* to the diazonium group.

In their influential review,[6] Bunnett and Zahler made it clear that the diazonium group was a particularly powerful member of a class of substituents which activate nucleophilic aromatic substitutions, which also includes the more familiar nitro group. They observed that the diazonium ion group was the most powerful activator known, in conformity with its very high σ-value.[7] Recently the rates of displacement of halogen *para* to the diazonium group by methoxide ion have been measured.[8] An exploratory experiment showed that the reactions of *p*-chloro- and *p*-fluorobenzenediazonium ion with thiocyanate ion were too slow to measure in water solution.[9] The contrast between this result and those of Hantzsch and his co-workers, and the first-order kinetics reported by Hantzsch for the chloride–bromide exchange prompted a more careful study of this system. The reactivity of thiocyanate in nucleophilic aromatic substitution was not questioned since it had been shown to displace either chloride[10] or the nitro group[11] to give 2,4-dinitrophenylthiocyanate; its reactivity in aliphatic substitutions is also well established.

Methods and Results

The reaction was followed by observing the introduction of radioactivity into the diazonium salt by reaction of a large excess of halodiazonium salt with carbon 14 tagged thiocyanate ion. Unreacted thiocyanate was removed to give a solution containing only the halo- and thiocyanatodiazonium ions, chloride and electrically neutral decomposition products. In some experiments the amount of radioactivity in these neutral products was determined by scintillation counting of a toluene extract at this stage. The apparent first-order rate constants divided by the diazonium ion concentration for the formation of these neutral decomposition products are referred to as the second-order constants, k_d. The diazonium salts were converted in good yield to the corresponding chloro compounds by reaction with cuprous chloride. These were extracted into toluene and counted in this solution, and gave the total amount of thiocyanate introduced into the molecule which ultimately became toluene soluble. Since most of the measurements were made without the prior extraction to determine k_d, the products counted include both chlorophenyl thiocyanate and the neutral decomposition products. The resulting apparent first-order constants, divided by the di-

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[1] Paper IV is E. S. Lewis and H. Suhr, *Chem. Ber.*, **93**, in press (1960).

[2] A. Hantzsch and B. Hirsch, *Ber.*, **29**, 947 (1896).

[3] B. Hirsch, *ibid.*, **31**, 1253 (1898).

[4] A. Hantzsch, *et al.*, (a) *ibid.*, **30**, 2334 (1897); (b) **33**, 505 (1900); (c) **36**, 2069 (1903).

[5] K. H. Saunders, "The Aromatic Diazo Compounds," Edward Arnold & Co., London, 1949, pp. 117–125.

[6] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

[7] E. S. Lewis and M. D. Johnson, THIS JOURNAL, **81**, 2007 (1959).

[8] B. O. Bolto, M. Liveris and J. Miller, *J. Chem. Soc.*, 750 (1956).

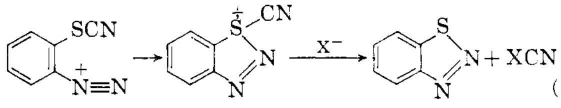
[9] R. E. Parker and E. S. Lewis, unpublished observations.

[10] P. T. Austin and F. S. Smith, THIS JOURNAL, **8**, 89 (1886).

[11] F. Challenger and A. D. Collins, *J. Chem. Soc.*, **125**, 1377 (1924).

azonium ion concentration, are the second-order constants for the total reaction, k_t. The second-order constant for the substitution reaction, k_s, was defined as $k_t - k_d$, and in a few cases was determined independently in experiments involving two extractions, one before and one after the cuprous chloride treatment, so as to count only the material which was rendered toluene soluble by cuprous chloride. In these cases k_s did not differ significantly from $k_t - k_d$. The introduction of radioactivity followed a first-order course, except as noted below, and the apparent first-order rate constant was proportional to the diazonium salt concentration.

This method follows the introduction of thiocyanate but does not identify the product. It was assumed that the *p*-halobenzenediazonium salts all gave ultimately *p*-chlorophenyl thiocyanate, since our conditions resemble those of Hantzsch,[2] who identified the product. With 2,4-dichlorobenzenediazonium ion and the 2,4,6-trichloro compound, the total activity is the sum of that due to substitution of the 2-chlorine and the 4-chlorine, with a negligible amount of disubstitution, since the dichloro compound was in large excess over the thiocyanate. The product of reaction of the simple *o*-substituted compounds is obscure. It was observed that the radioactivity change did not follow a first-order course, but instead increased to a maximum and then decreased, as illustrated in Fig. 1. This indicates that the initial reaction product lost the thiocyanate carbon to a water-soluble, toluene-insoluble or volatile form. We believe that the introduction of radioactivity followed the same course as it did in the *para* case to give the *o*-thiocyanatobenzenediazonium ion, but that this was unstable under the reaction conditions. The ultimate product was not identified; a possibility that benzothiadiazole was formed through reaction 1 was eliminated since the absorption spectrum of the product did not show the characteristic maxima of benzothiadiazole. The possibility that the entire thiocyanate group was displaced by water was not ruled out. This deviation from a first-order course was apparently most serious with the *o*-iodo and *o*-bromo compounds.



(1)

Preliminary results established the kinetic law, the approximate magnitude of the salt effects and some qualitative solvent effects and substituent effects.

The 2,4,6-trichlorobenzenediazonium ion in water solution gave apparent first-order rate constants varying by a factor of 2.1 for a change in diazonium ion concentrations of a factor of 1.9. Over this range the second-order rate constants were 0.011, 0.011 and 0.012 l./mole.sec. at 30°, confirming the second-order law. Some less accurate results on the *o*-chloro compound in 95% *t*-butyl alcohol showed again that the second-order rate constant, now uncertain to about ±15%, was unaltered by a factor of two change in diazonium ion concentration. There is no suggestion that any other rate law (such as the first-order law of ref. 4) would be as satisfactory.

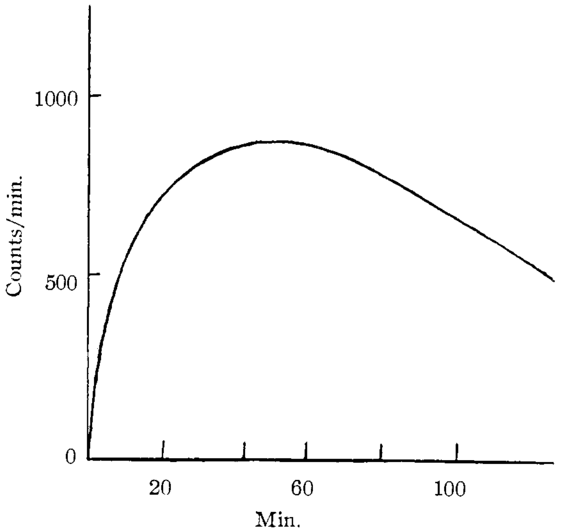


Fig. 1.—Dependence of counting rate of product samples on time of reaction of *o*-iodobenzenediazonium ion with thiocyanate.

In *ca.* 0.01 M solution in water, 2,4,6-trichlorobenzenediazonium ion reacted with 2×10^{-5} M thiocyanate at a rate uninfluenced by sulfuric acid (4×10^{-3} M), hydrochloric acid (4×10^{-3} M), sodium chloride (2×10^{-3} M), but the rate was retarded about 30% by 0.4 M sodium nitrate. Cupric sulfate (10^{-4} M) and pyridine (10^{-4} M), did not influence the rate. The rate referred to in every case is the total rate, given by k_t. Rate constants for other conditions are given in Tables I through IV.

TABLE I

RATES OF 2,4-DICHLOROBENZENEDIAZONIUM ION WITH THIOCYANATE IN AQUEOUS METHANOL AT 20°

Solvent, wt. % MeOH	Dielectric constant	k_t, l./mole sec.
25	74.0	0.00125
50	56.5	.0027
70	47.3	.014
90	37.3	.087
98	33.3	.30

Table I shows the effect of water in methanol on the rate of reaction of 2,4-dichlorobenzenediazonium ion. In water alone the total rates (k_t) for the 2,4,6-trichloro compound, the 2,4-dichloro and the 2,5-dichloro compounds are, respectively, 0.01, 0.00063, 0.0006, and the *p*-chloro compound reacts too slowly to measure. The correction for decomposition is large in the last two numbers, so that k_s is not known with good precision.

Table II shows the rates of the *p*-bromobenzenediazonium salts with thiocyanate in various *t*-butyl alcohol mixtures.

Table III shows corresponding figures for the reactions of *o*-chlorobenzenediazonium ion with thiocyanate at 20°, showing also the solubility of the fluoroborate salts in the same solvent.

The variation of rate with solvent is regular, and as shown for the case of the *p*-bromo and *o*-chloro compounds in Fig. 2, follows with reason-

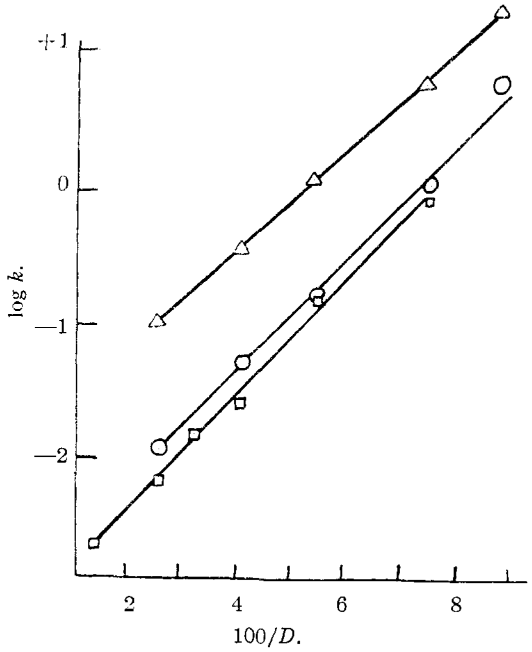


Fig. 2.—Dependence on dielectric constant in aqueous *t*-butyl alcohol: △, *p*-bromobenzenediazonium fluoroborate, k_t for reaction with thiocyanate; ○, *o*-chlorobenzenediazonium fluoroborate, k_t for reaction with thiocyanate; □, same, $10^4/K_{s.p.}$

able precision the expected linear relation between the logarithm of the rate constant and the reciprocal of the dielectric constant. A very similar effect on the halogen exchange was noted by Hantzsch.[4b] The logarithm of the equilibrium constant (the reciprocal of the solubility product of the solid salt) for reaction 2 is also plotted in the figure.

$$o\text{-ClC}_6\text{H}_4\text{N}_2{}^+ + \text{BF}_4{}^- \rightleftarrows o\text{-ClC}_6\text{H}_4\text{N}_2{}^+\text{BF}_4{}^-\text{(cryst.)} \qquad (2)$$

The near linear relation and the similar slope to that of other lines suggests that the activity coefficient of the electrically neutral transition state for the substitution reaction is insensitive to solvent, as is of course the activity of the solid diazonium salt. It is not clear whether the use of solubility equilibria can be considered as a generally useful model for reactions of ions passing through uncharged transition states.

Table II

Reaction Rates of *p*-Bromobenzenediazonium Ion with Thiocyanate at 20°

Solvent, wt. % *t*-butyl alc.	Dielectric constant	l./mole sec. k_t	k_d	k_s
95	11.5	0.30	0.016	0.28
90	13.5	.090	.013	.077
80	18.8	.018	.0015	.016
70	25.3	.0053	.0003	.0050
50	40.0	.0016	.0002	.0014

Table III

Reaction Rates of *o*-Chlorobenzenediazonium Ion with Thiocyanate at 20°

Solvent, % *t*-BuOH	l./mole sec. k_t	k_d	k_s	Solubility of *o*-$\text{ClC}_6\text{H}_4\text{N}_2\text{BF}_4$, moles/l. × 10^2
95	0.083	0.0017	0.082	...
90	.016	.0008	.015	1.19
80	.0023	.0005	.0018	2.70
70	.00077	.0002	.0006	6.70
60	.....	....	....	8.60
50	.00017	....	....	12.7
0	.....	....	....	21.0

Table IV

Reaction Rates of Several Diazonium Ions with Thiocyanate in 95% *t*-Butyl Alcohol

Substituent	Temp., °C.	k_t	k_d	k_s
p-F	20.0	0.0012	0.0003	0.0009
p-Cl	10.6	.0092	.0002[a]	.007
p-Cl	20.0	.019	.0007[a]	.018
p-Cl	30.0	.090	.0027[a]	.063
p-Br	20.0	.31	.01	.30
p-I	20.0	.39	.008	.38
p-NO_2	20.0	.0080	.0025	.0055
o-F	20.0	.04	.03	.01
o-Cl	20.0	.08	.02	.06
o-Br	20.0	.25	.06	.19
o-I	20.0	.13	.04	.09

[a] The apparently anomalous temperature dependence of k_d is probably an indication of low reproducibility, rather than a real anomaly.

Table IV shows the effect of changing the position and nature of the halogen. In addition to the results reported there, experiments on several *m*-substituted compounds failed to detect any substitution reaction, which showed that this reaction was not more than one one-hundredth as fast as that of the *p*-fluoro compound, the least reactive compound with a measurable rate. The precision of the total rate k_t for the *p*-Cl, *p*-Br and *p*-I cases is about ±10%, and about ±20% for the *p*-F compound, which was not followed to a very large extent of completion. The error on the compounds with *o*-halogen is difficult to estimate for the reason stated previously. We are confident that the rate is accurate to within a factor of two; the reproducibility of the initial rates was much better than this. The numbers given for k_t are the averages of the results of two or three runs. The deviations from the mean are within the errors estimated above.

Discussion

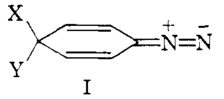
The Kinetic Law.—The reaction in water solution is clearly first order in each of the two ions, and the same rate law is indicated for the reaction in the other solvents, although the order in the diazonium ion is not so rigorously demonstrated. These arguments apply specifically to the over-all reaction, but in most cases the substitution predominates so that the argument applies also to k_s. It appears that the same law applies for the decomposition process. The similarity of the solvent effects k_t and k_d suggests that both are reactions of an anion with a cation, and therefore the same rate law for the two reactions is indicated more strongly by the solvent effects than by the individual rate studies. A kinetically second-order but mechanistically complicated reaction between benzenediazonium ion and thiocyanate ion to give phenyl thiocyanate has been suggested by Cooper.[12] This presumed free-radical process may well be even more important with substituted benzenediazonium ions; our data here are insufficient to see if the erratic behavior observed by Cooper also exists here.

The Solvent Effect.—The effect of changing solvents is just as might be expected for a reaction between two oppositely charged ions. The reasonable correlation with dielectric constant alone suggests that the transition state does not contain solvent molecules playing any very important specific roles. The apparent discrepancy between our preliminary results and the very rapid reaction observed by Hantzsch and Hirsch is now clear. Doubtless the very fast reaction first observed occurred almost exclusively after the alcoholic solution of *p*-chlorobenzenediazonium thiocyanate was diluted with ether to precipitate the salt.

Since the rates are very dependent on solvent, it is quite unjustifiable to compare quantitatively the activating influence of the diazonium group with that of the more traditional neutral activating groups. Nevertheless, the rate constants are impressively high. Thus the reaction of 2,4-dinitrochlorobenzene with thiocyanate is carried out at 60–80°, and there are no reactions of singly activated halobenzenes carried out at such low temperatures, so the qualitative statement[6] that the diazonium ion is the most powerfully activating group for nucleophilic aromatic substitution is certainly justified.

The Effect of Position and Nature of the Halogen.—The majority of reported examples of substitution are those of groups *ortho* to the diazonium group, rather than *para*, suggesting that the rate at the *o*-position is much faster than at the *p*-position.[5] The sterically similar and isoelectronic reactions of halobenzonitriles show about the same *ortho* and *para* reaction rates with piperidine; the nitro activated halobenzenes react with piperidine more rapidly in the *ortho* case than in the *para*, but with methoxide in the *p*-nitro compound is the more reactive.[13] It is therefore not surprising that the rate of reaction of *o*-chlorobenzenediazonium ion is only slightly faster than that of its *p*-isomer. The same order prevails in the fluorine substituted compounds, but the bromine and iodine compounds may be reversed, the uncertainties in the rates of the *ortho* compounds prevents a more precise analysis.

The Reactivity of the Halogens.—Table IV shows that in the *para* series the order is F < Cl < Br < I. This is somewhat unusual in nucleophilic aromatic substitution, but not unprecedented.



I

We attribute this order to two primary factors, and admit the possibility of further factors which at present seem less important. One factor in the high reactivity of the iodine compound is the high polarizability of both the iodide and the thiocyanate ions. If we assume the intermediate I for the attack of Y^- on *p*-X-benzenediazonium ion, the energy *vs.* reaction coördinate curve for the complete reaction will show a minimum at the configuration I. On leaving this minimum in either direction the energy of the adjacent transition state will be lowered if the leaving group is highly polarizable, so that substantial bond energy may persist at long bond distances. The lowering of the energy of the transition state with the bond to the polarizable group incompletely formed will bring this transition state in all respects closer to the intermediate.[14] If the bond to the leaving group X is also polarizable, then by the same argument the second transition state is also close to the intermediate, and therefore both transition states will have contributions of structures in which both bonds are broken, and hence the bond strength to the leaving group can be reflected in the reaction rate if the attacking group is polarizable. Thus the highly polarizable thiocyanate ion reagent will be expected to have a smaller ratio k_F/k_I than would be found with a first-row atom as a nucleophile.

A second factor may be found in the nature of the solvent. The fluoride ion, by virtue of its small size and basic character, must be solvated by hydrogen bonding to a more important extent than other halides. Thus hydrogen bonding can be expected to play an important part in substitution reactions with a fluoride leaving group. Part of the low reactivity of the fluoride in the reaction considered here may be due to the very low acidity and hydrogen-bonding capacity of the *t*-butyl alcohol solvent.

Another factor which may contribute to the reversed order of halogen reactivities is that the attacking group is, by virtue of its linearity, not likely to interfere seriously even with a leaving iodine so that the transition state is not seriously hindered. Finally, the very great electron-withdrawing power of the diazonium group may make the lesser electron withdrawal by fluorine negligible, so that the usual reasons for extra reactivity of fluorine compounds do not exist. This "saturation" of the electron-withdrawing effect certainly does not appear on going from mononitrohalobenzenes to 2,4-dinitrohalobenzenes, but it may nevertheless be significant with still more extensive electron withdrawal. A closely related effect resulting from extreme electron withdrawal would be the retarding effect of contribution to the initial state of structures with a double bond to halogen. This would be of importance only with fluorine.

In sum, the high polarizability of the attacking thiocyanate and its modest steric requirements, the poor hydrogen bonding characteristic of the solvent *t*-butyl alcohol, and the extreme electron-withdrawing power of the diazonium group can all be reasonably expected to contribute to the inversion of the usual order of the halogens. The nitro group occupies a position between chlorine and fluorine as it also does in cases where the fluoro compound is more reactive than the chloro compound.

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[12] J. E. Cooper, Thesis, The Rice Institute, 1959.

[13] The pertinent data are summarized in a Table XIV in the volume edited by M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 190.

[14] G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

We may conclude that this reaction is a normal activated substitution passing through the structure I.

Experimental

Materials.—The diazonium salts were prepared in the usual manner from the corresponding amines, which were commercial materials, and were precipitated by the addition of 10% fluoroboric acid. They were recrystallized by dissolving in ethanol at room temperature, then cooling to −40°. Two recrystallizations usually sufficed to give material which gave ultraviolet spectrum and reaction rates unaltered by further recrystallization. Carbon 14 labeled sodium thiocyanate (obtained in allocation-free quantities from Merck and Co. of Canada) was diluted to a specific activity of about 100 μc. per g. Stock solutions of this were made up in water for the work in water solution and in dimethoxydiethyl ether for all other solvents.

Kinetics.—Solutions of appropriate concentration were made up and placed in the thermostat, which regulated the temperature to better than ±0.2°. Ten-ml. samples were then treated by two different methods to remove unreacted thiocyanate; the resulting solutions were then added to 25 ml. of a solution of excess cuprous chloride in hydrochloric acid. After at least two hours at room temperature, the mixture was extracted with 25 ml. of reagent grade toluene, using a shaking machine for 10 minutes, and the extract was then washed with 25 ml. of water. After drying over calcium chloride, 10 ml. of the solution was mixed with 10 ml. of a solution containing 3 g. of 2,5-diphenyloxazole and 0.1 g. of 1,4-di-(2-(5-phenyloxazolyl))-benzene per liter, then counted in a Packard Tri Carb Scintillation spectrometer using conventional settings. For the slowest reactions at least 1000 counts were recorded, and for most of the runs at least 10,000 counts were recorded. Activities were well above background in all cases so that minor changes in the background could not cause error comparable with that from other sources. Several representative samples were tested for quenching by adding known amounts of radioactive benzoic acid. The rate of counting was indeed lower by about one-quarter than in pure toluene with the standard benzoic acid. This quenching was reproducible and no correction was necessary, since the reactions followed a first-order course. With the *o*-fluoro and *p*-nitro compounds colored by-products were formed, leading also to an optical quenching. Corrections were applied in these cases.

The constant k_d was determined from the counting rates of toluene extracts made before the cuprous chloride treatment. Since it was measured only to show that the correction was small, only about two points were taken and the precision is low.

Neither of the two methods for removing radioactive thiocyanate from the solution gave a quantitative recovery of radioactive diazonium salt, but both were reproducible in this respect. In the first method, 10 ml. of the reaction mixture was diluted with 100 ml. of cold water and 1 millimole of inactive sodium thiocyanate was added. A small excess of silver nitrate was then added and the solution filtered, then treated with cuprous chloride. Only about 45% of the maximum expected number of counts could be obtained by this method. In the second method, a 10-ml. sample of the reaction mixture was diluted with 40 ml. of cold water and passed through a chloride form anion exchange resin (Amberlite IRA-400) in a column cooled from the outside to 6°. The column was washed with 110 ml. of cold water and the solution treated as before with cuprous chloride. This gave about 60% of the expected number of counts. The majority of the runs was done using the second method. Second-order rate constants were calculated by dividing the apparent first-order rate constants by the initial diazonium ion concentration. The apparent first-order rate constants were the slopes of plots of ln $N_\infty/(N_\infty - N_t)$ *vs.* time, where N_t and N_∞ are the counting rates of samples at time *t* and after many half-lives. Both separation methods gave good straight lines in this plot, and the slopes were the same.

Dielectric constants were measured using a Sargent Oscillometer.[15] A plot of dial reading *vs.* reciprocal of the dielectric constant for several known liquids was linear, so that interpolation was straightforward. Measurements were made at room temperature.

Solubility measurements were made by stirring solid diazonium fluoroborate with the solvent in a thermostat for 20 minutes, then centrifuging to remove the solid; the clear solution was appropriately diluted with water and the concentration determined by measuring the ultraviolet absorbance at the maximum. Since large dilutions were made, no correction for change in spectrum with solvent was made. The values in Table III are the averages of at least three determinations, including some made by adding a saturated water solution with solid salt to the *t*-butyl alcohol solvent so as to approach the equilibrium from the super-saturated side.

Acknowledgment.—We wish to thank the Robert A. Welch Foundation for support of this research.

[15] We thank the Research and Development department of the Humble Oil and Refining Co. for the use of this instrument.

HOUSTON, TEX.

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO.]

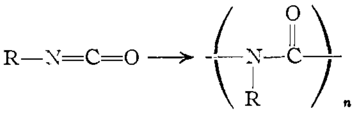
The Homopolymerization of Monoisocyanates

BY VICTOR E. SHASHOUA, WILFRED SWEENY AND RAYMOND F. TIETZ

RECEIVED JULY 1, 1959

Monoisocyanates were polymerized at low temperatures (−20 to −100°) by anionic catalysts to give linear high molecular weight polymers. These polymers are classified as 1-nylons. The reaction is applicable to both aliphatic and aromatic isocyanates. The scope and limitations of the reaction are defined. The properties of the 1-nylons are described. A proposed mechanism for the reaction is given.

The formation of cyclic dimers and trimers from isocyanates is a well known reaction, promoted by such basic reagents as triethylamine,[1] triethylphosphine[2] and pyridine.[3] In a previous communication[4] from these laboratories the homopolymerization of monoisocyanates to linear film forming products was demonstrated. These studies have now been extended to a host of aliphatic and aromatic isocyanates in an attempt to examine the scope and limitations of this new reaction of isocyanates. To our knowledge the homopolymerization of isocyanates in accordance with the reaction scheme below represents the first example of the polymerization of compounds with $>C{=}N{-}$ groups to high molecular weight products. These



$$\mathrm{R{-}N{=}C{=}O} \longrightarrow \left({-}\underset{\mathrm{R}}{\underset{|}{\mathrm{N}}}{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-} \right)_n$$

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[1] D. H. Chadwick and T. C. Allen, U. S. Patent 2,733,254 (1956).

[2] A. W. Hofmann, *Ber.*, **3**, 761 (1870).

[3] H. L. Snape, *J. Chem. Soc.*, **49**, 254 (1886).

[4] V. E. Shashoua, THIS JOURNAL, **81**, 3156 (1959).