near-dryness under reduced pressure to yield a white solid. Addition of 25 ml. of absolute ethanol, then evaporation to about 20 ml. and addition of 20 ml. of isoamyl alcohol gave 4.0 g. (50%) of product, which was washed with ether, m.p. 210–211°. A melting point of 206° was reported by Davis and Elderfield.[13]

Morpholinecarboxamidine Sulfate.—Methylisourea sulfate (6.15 g., 50 meq.) and morpholine (7.5 g., 86 meq.) were mixed in 30 ml. of 50% methanol. After standing at 25–30° for 36 hours, 3.3 g. of prisms separated. The solution was evaporated and ethanol was added to yield 3.0 g., total 6.3 g. (70%), m.p. 306° dec.

Anal. Calcd for $C_{10}H_{24}O_6N_6S$: S, 9.00; N, 23.6. Found: S, 9.02; N, 23.0.

d-Bornylguanidine Sulfate.—When this compound was first prepared with stoichiometric quantities under conditions similar to those for butylguanidine sulfate, the reaction was about 75% complete in 12 hours, but the precipitate contained some *d*-bornylamine sulfate, as indicated by titration to an alizarin yellow end-point, and confirmed by a low nitrogen content. It proved difficult to remove this impurity, so the reaction was repeated, this time with excess methylisourea as follows: *d*-bornylamine (3.5 g., 22.8 meq.) in 30 ml. of methanol was treated with methylisourea sulfate (4.07 g., 33 meq.), and enough barium hydroxide solution to remove the 10 excess meq. of sulfate ion. After a brief warming, the solution was filtered from barium sulfate and concentrated. Cooling yielded 1.5 g. of precipitate which, after recrystallization from 90% methanol, gave no titration to the alizarin yellow end-point, m.p. 326–330° dec., $[\alpha]^{28}D$ +21.4 ± 0.6° (3.5% in 50% ethanol).

Anal. Calcd. for $C_{20}H_{44}O_4N_6S$: S, 6.5; N, 17.2. Found: S, 6.4; N, 17.1.

Acknowledgment.—Thanks are expressed to Mr. A. J. McMillan for analyses performed.

AMES, IOWA

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[13] T. L. Davis and R. S. Elderfield, THIS JOURNAL, **54**, 1499 (1932).

[CONTRIBUTION FROM THE JET PROPULSION LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Rate of Addition of the Nitrate Ion to the Ethylene Oxide Ring[1]

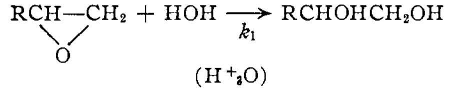
BY WALTER L. PETTY AND PETER L. NICHOLS, JR.[2]

RECEIVED APRIL 23, 1954

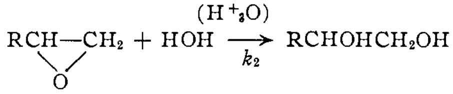
The rate of addition of the nitrate ion to several oxides has been measured under neutral and acidic conditions in aqueous solution. A rapid method for determining the rate of the uncatalyzed reaction was developed. The nucleophilic tendency of the nitrate ion is discussed in terms of Swain's rate correlation equation. Acid-catalyzed rate constants determined in solutions of high salt concentration gave a prediction of yield data under conditions favorable for synthesis of nitric esters

Previous investigators[3,4] observed that the nitrate ion adds to the ethylene oxide ring in aqueous solution; however, no reasonably accurate rate data were obtained by them. Part of the difficulty was caused by the slow rate of addition of the nitrate ion as compared with the competing hydrolytic reaction. For this investigation, conditions were chosen which made it possible to determine the rate of addition of the nitrate ion to several oxides in both neutral and acid solutions. Moreover, rough rate measurements were made with ions even more weakly nucleophilic than the nitrate ion.

The major reactions occurring in aqueous solution when an unsymmetrical oxide reacts with the nitrate ion are[5]



(A)



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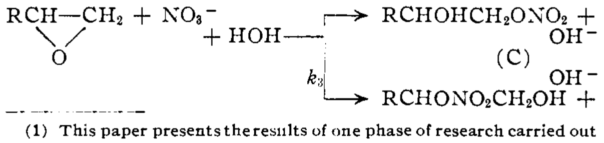
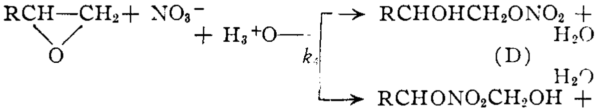


(C)



(D)

Under the conditions used to obtain the kinetic data, the primary nitric ester was formed predominantly, except for propylene oxide where a mixture of the two isomers was produced.[5,6]

The fractional rate of oxide disappearance is

$$-\,d(E)/(E)dt = k_1(HOH)^2 + k_2(HOH)(H_3{}^+O) + k_3(NO_3{}^-)(HOH) + k_4(NO_3{}^-)(H_3{}^+O) \quad (1)$$

where (E) = concentration of oxide (moles liter), (HOH) = concentration of water (moles liter), (NO_3^-) = concentration of nitrate ion (moles/liter), and $(H_3{}^+O)$ = concentration of hydronium ion (moles/liter). In equation 1 third-order rate constants are employed since they are believed to be consistent with the over-all kinetics of each reaction. Some of the values of k_1 and k_2 for the oxides studied had already been determined.[3] It was then necessary to choose conditions whereby the individual values of k_3 and k_4 for various oxides could be determined.

Experimental

Materials.—Reagent-grade sodium salts of the various ions tested were used without further purification. Epibromohydrin was obtained from Eastman Kodak Co., and epichlorohydrin and allyl glycidyl ether from Shell Chemical Co. Glycidol was prepared by the reaction of glycerol α-monochlorohydrin and alcoholic sodium ethoxide as described by Rider and Hill.[7] All of the oxides were distilled under vacuum through a 1-foot column filled with Podbielniak "Heli-pak" random packing.

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[1] This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. DA-04-495-Ord 18, sponsored by the Department of the Army, Ordnance Corps.

[2] To whom inquiries regarding this article should be sent.

[3] J. N. Brönsted, M. Kilpatrick and Martin Kilpatrick, THIS JOURNAL, **51**, 428 (1929).

[4] L. Smith, G. Wode and T. Widhe, *Z. physik. Chem.*, **130**, 154 (1927).

[5] P. L. Nichols, Jr., J. D. Ingham and A. B. Magnusson, THIS JOURNAL, **75**, 4255 (1953).

[6] J. D. Ingham and P. L. Nichols, Jr., *ibid.*, **76**, 4477 (1954).

[7] T. H. Rider and A. J. Hill, *ibid.*, **52**, 1521 (1930).

Glycidyl Nitrate.—Over a period of 1.5 hours, 500 ml. of 10 *M* sodium hydroxide solution was added to a well-stirred mixture of 780 g. (5 moles) 1-nitrato-3-chloropropanol-2 (synthesis described in ref. 3) and 600 ml. of water. The mixture was stirred for an additional 10 minutes, and the lower layer of crude glycidyl nitrate was separated. The aqueous layer was extracted twice with 250-ml. portions of ether, and these were combined with the main product and dried over anhydrous sodium sulfate. The ether was removed under vacuum, and the product distilled through a 2-foot Vigreux column; yield 429 g. or 72%, b.p. 65-66° (9 mm.), $n^{25}\text{D}$ 1.4340.

The glycidyl nitrate used in the kinetic measurements was obtained by careful distillation of some of the above product through the Podbielniak column mentioned previously, b.p. 40.9-41.0° (2.5 mm.), $n^{20}\text{D}$ 1.4359.

Anal. Calcd. for $C_3H_5NO_4$: N, 11.76. Found: N, 11.90.

Uncatalyzed Addition of Nitrate Ion to Oxides.—Approximately 1 g. of oxide was added to 100 ml. of a solution of the salt to be tested (dissolved in boiled, distilled water). This mixture was shaken until the oxide dissolved, and then it was acidified with a few drops of dilute acid to about a *p*H 4. This solution was stirred in a 100-ml. flask which was immersed in a constant temperature bath, 25.0 ± 0.1°, and the *p*H of the solution was measured at frequent time intervals with a Beckman model G *p*H meter, reading to ±0.01 *p*H unit.

From the *p*H change in the solution the amount of reaction was calculated. By plotting the amount of reaction *vs.* time, the rate constant was obtained from the slope of the resulting curve. (The concentrations of the reactants are considered constant since a negligible amount of reaction takes place over the *p*H range measured.)

Acid-catalyzed Reaction of Nitrate Ion with Oxides.—Five to ten grams of the organic oxide to be tested was added to 300 ml. of a nitric acid–sodium nitrate solution in a 500-ml. flask. This mixture was shaken so that the oxide would dissolve quickly, and the flask was placed in a constant temperature bath, 20.0 ± 0.1°. At convenient time intervals 10-ml. aliquots of this solution were removed, diluted with 100 ml. of water, and quickly titrated with standard sodium hydroxide solution. The rate of formation of nitric ester was calculated from the change in acid concentration by a method described later.

Discussion

Uncatalyzed Rate Constants (k_3).—In nearly neutral aqueous solutions reaction D usually proceeded slowly as compared with reaction C. If mild interference from reaction D was encountered, corrections could be applied as was true of glycidol. However, in the case of epiiodohydrin and propylene oxide, reaction D so overshadowed reaction C in the desired *p*H range that an accurate measurement of reaction C was not possible. The general nature of the experimental curves for the addition of bromide ion to glycidol is shown in Fig. 1. Curves obtained in this manner often exhibited as many as four distinct regions: region I which is characterized by the fact that some of the *p*H changes are due to the acid-catalyzed reaction D; region II which represents reaction C; region III in which the *p*H has reached the point where carbon dioxide dissolved in solution begins to interfere by partial neutralization of the base formed in the reaction and where a rough calculation showed that a carbon dioxide concentration as low as 10^{-6} molar would produce a noticeable effect; and, as the solution approached the basic side, region IV which exhibited a retardation in rate as a result of the reversal of the addition reaction. An excellent discussion of the reversible nature of these reactions is found in ref. 8. On the basis of these considerations it was decided to use data between *p*H 4 and 5.4 for calculation of k_3 constants.

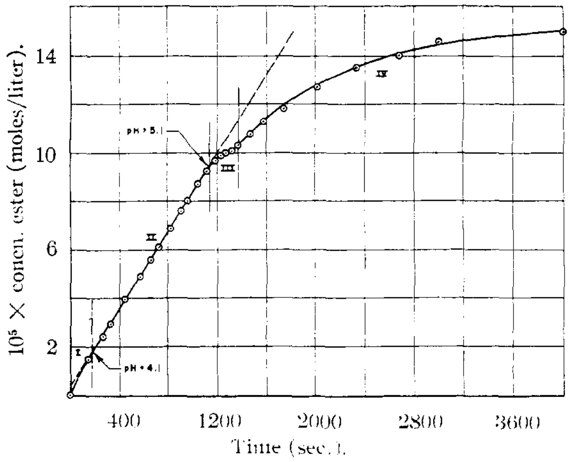

Fig. 1.—Uncatalyzed reaction of bromide ion with glycidol; composition of solution: 0.111 *M* glycidol, 0.0464 *M* sodium bromide.

As a result of the side reactions which have been discussed, it was necessary to check a few rate constants determined by this method with those obtained by a more straightforward method.[3] Therefore, some comparative data on other ions have been included in Table I along with the corresponding nitrate ion additions. Attempts were made to determine the uncatalyzed addition rates of chlorate, bromate, iodate and perchlorate ion (all in saturated solutions of their respective salts) to propylene oxide. It had previously been indicated[3] that perchlorate ion has essentially no nucleophilic tendency. With the sole exception of bromate ion, the results show the k_3 rate constants to be less than 10^{-10}. The experimental data for bromate ion suggested that $k_3 = 6 \times 10^{-9}$; however, a trace of bromide ion easily could have obscured the results. In fact, by this method small quantities of bromides in bromates might be determined.

The rate constants for the addition of nitrate ion to epichlorohydrin at three different salt concentrations showed a salt effect $(1/k_3^0)(\mathrm{d}k_3/\mathrm{d}c)$ of about -0.2. This value agrees with that obtained by Brönsted[3] for the addition of chloride, bromide and iodide ions to epichlorohydrin and glycidol. The rate constants for the uncatalyzed reactions at zero salt concentration, $k_3{}^0$, were calculated for the five oxides tested, assuming that the same salt effect holds true for all.

Acid-catalyzed Rate Constants (k_4).—In order to provide the appropriate expressions for calculation of the acid-catalyzed rate constants k_4, the following definitions will be required where all concentrations are expressed in moles/liter: E_0, initial oxide concentration; E, oxide concentration; N_0, is initial nitrate ion concentration; N, nitrate ion concentration; H_0, initial hydronium ion concentration; H, hydronium ion concentration; W_0, initial water concentration; W, water concentration; n, nitric ester concentration; g, glycol concentration, and r is k_4/k_2.

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(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 243.

TABLE I

UNCATALYZED RATE CONSTANTS (k_3)[a]

Oxide	Chloride[b] ion Measured $k_3^0 \times 10^6$	Chloride[b] ion Brönsted[d] $k_3^0 \times 10^6$	Bromide[b] ion Measured $k_3^0 \times 10^6$	Bromide[b] ion Brönsted[d] $k_3^0 \times 10^5$	Salt concn., mole/liter	Nitrate[c] ion Measured rate at given concn. $k_3 \times 10^8$	Calcd. rate at zero concn.[e] $k_3^0 \times 10^8$
Glycidol	2.6	2.5	1.6	1.7	0.983	5.38	6.7
					.992	5.37	
					.983	20.7	
					.981	21.1	
Epichlorohydrin	9.9	11	6.3	6.2	.980	21.2	26
					.569	22.6	
					.391	22.9	
Allyl glycidyl ether	..	..	..	..	.991	10.1	13
Glycidyl nitrate	..	..	..	..	.990	18.0	22
					.990	19.6	
Epibromohydrin	..	..	..	..	.989	19.8	25

[a] These were calculated as second-order rate constants, the units being liters/mole-second. [b] Measured at 20.0°. [c] Measured at 25.0°. [d] *Cf.* ref. 1. [e] It is assumed that the salt effect, $(1/k_3^0)(\mathrm{d}k_3/\mathrm{d}c) = -0.2$, is approximately true for all of the oxides.

In experiments relating to the determination of k_4 the oxide concentration employed was such that only nitric ester and glycol were formed. The concentration of oxide was sufficiently small to approximate $(W_0 - g)$ by W_0. Finally, the experimental conditions were such that $k_4H >> k_3$ and $k_2H >> k_1$. Therefore, the equation for the disappearance of oxide with time can be presented as

$$-\,\mathrm{d}E/\mathrm{d}t = k_2HEW_0 + k_4HEN \tag{2}$$

Expressions for the appearance of nitric ester and glycol are

$$\mathrm{d}n/\mathrm{d}t = k_4HEN \tag{3}$$

and

$$\mathrm{d}g/\mathrm{d}t = k_2HEW_0 \tag{4}$$

By dividing equation 4 by equation 3 and by rearranging and integrating the resulting expression, relation 5 is obtained

$$g = \frac{W_0}{r}\ln\left(\frac{N_0}{N_0 - n}\right) \tag{5}$$

It is assumed that $E_0 = n_f + g_f$, where n_f and g_f are the nitric ester and glycol concentrations for complete reaction. The quantity r can now be evaluated from the equation

$$r = \frac{W_0}{E_0 - n_f}\ln\left(\frac{N_0}{N_0 - n_f}\right) \tag{6}$$

A mass balance combined with the use of equation 6 gives the expression

$$E = E_0 - n - \frac{W_0}{r}\ln\left(\frac{N_0}{N_0 - n}\right) \tag{7}$$

Expanding the logarithmic term, neglecting all terms but the first, and combining equations 3 and 7 results in a differential equation with the solution

$$k_4t = \frac{A}{DE_0}\left[(N_0 - A)\ln\left(\frac{H_0}{H_0 - n}\right) + (H_0 - N_0)\ln\left(\frac{A}{A - n}\right) + (A - H_0)\ln\left(\frac{N_0}{N_0 - n}\right)\right] \tag{8}$$

where

$$A = E_0/(1 + W_0/rN_0)$$
$$D = (H_0 - A)(H_0 - N_0)(N_0 - A)$$

Values of k_4 were obtained by plotting the right-hand side of equation 8 against t, and k_4 was then calculated from the initial slope of the resulting curve. In a few cases the values of n/N_0 were sufficiently large to necessitate inclusion of the square term in the logarithmic expansion. The differential equation which resulted was solved in a straightforward manner; however, the lengthy algebraic expression of the solution is not given here.

Data obtained on k_4 constants for the addition of nitrate ion to several oxides are shown in Table II. In Fig. 2 the effect of salt concentration on the k_4 constant is demonstrated. It is significant that the salt effect calculated for the k_2 constants at high concentrations agreed with that obtained by Brönsted, *et al.*,[3] at low concentrations, as shown in Fig. 3. This agreement suggests consistency between the independent determinations, and, moreover, reveals that there is a linear relationship between the k_2 constant and ionic strength over a very wide concentration range. Although linear relationships of this type are well known for reactions between an ion and a neutral molecule,[9] attempts at their theoretical justification are not completely satisfactory. The variation of k_4 constants in the high ionic strength solutions em-

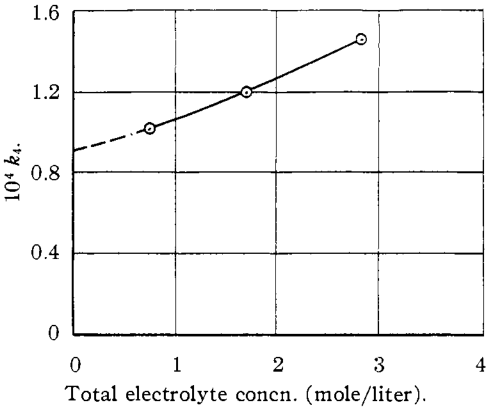

Fig. 2.—Effect of electrolyte concentration on acid-catalyzed reaction rate of nitrate ion and epichlorohydrin.

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(9) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 441.

TABLE II

ACID-CATALYZED RATE CONSTANTS (k_4 AND k_2)[a]

Oxide	Concn. range[b] of electrolyte c = (HNO_3) + ($NaNO_3$), moles/liter	Nitrate addition rate constant, $k_4 \times 10^5$	Hydrolysis rate constant $k_2 \times 10^6$	
			Calcd.[c]	Brönsted[d]
Glycidol	1.2–4.4	$55(1 + 0.20c)$	$47(1 + 0.50c)$	$44(1 + 0.55c)$
Epichlorohydrin	0.75–2.8	$9.0(1 + 0.22c)$	$7.4(1 + 0.54c)$	$7.3(1 + 0.61c)$
Propylene oxide	1.2–3.2	$410(1 + 0.44c)$	$480 (1 + 0.83c)$	....

[a] These were measured at 20.0° and calculated as third-order rate constants, the units being (liters^2/moles^2-second). [b] Determinations were made at four different concentrations for glycidol and propylene oxide and at three different concentrations for epichlorohydrin. [c] Using the ratio of nitric ester to glycol formed in the reaction and the k_4 value, it was possible to calculate k_2. [d] Hydrolysis rate constants in very dilute solutions; *cf.* ref. 1 (converted from second-order to third-order rates).

ployed here was in the opposite direction to that observed for other ions in very dilute salt solution ($\mu \leqq 0.04$).[3]

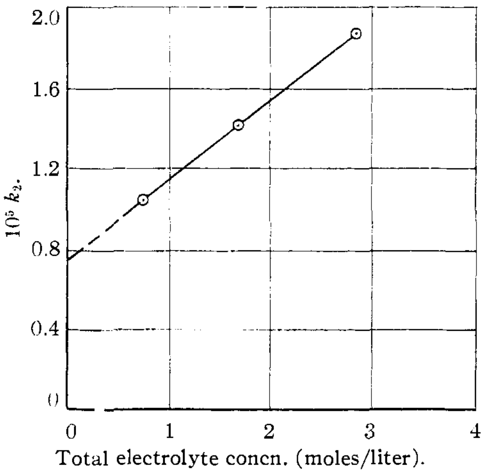

Fig. 3.—Effect of electrolyte concentration on the acid-catalyzed hydrolysis rate of epichlorohydrin.

Rate Correlations.—In an interesting paper by Swain and Scott[10] the following equation was proposed for the quantitative correlation of relative rates of nucleophilic displacement reactions

$$\log k/k^0 = sn \qquad (9)$$

where

k = rate constant for nucleophilic displacement reaction involving nucleophilic reagent and water
k^0 = rate constant for nucleophilic displacement involving water alone
s = a constant characteristic of the given substrate (in the present case an oxide)
n = a constant characteristic of a given nucleophilic reagent

This linear free-energy relationship is of the same general type as of the original Hammett equation.[11] In Table I of the paper by Swain and Scott a minor error (rate constant k off by a factor of 2.3) occurred in the calculation of k/k^0 for the reaction of glycidol with several ions. The correct values of $\log k/k^0$ for glycidol with Cl^-, Br^-, I^- and SCN^- ions are 2.70, 3.53, 4.73 and 4.41, respectively. These values have been calculated using data from Brönsted, *et al.*[3]

This correction necessitates a slight revision of the curves included in the Swain and Scott paper and a consequent adjustment of the nucleophilic and substrate constants calculated therein. However, this revision tends to improve rather than to detract from the correlation of Swain and Scott, especially in the case of β-propiolactone. An important result of the change is a reversal in the order of substrate constants for glycidol and epichlorohydrin, their new values being, respectively, 0.96 and 1.00. The change in order is in agreement with the results of this paper. The rate correlation curves for glycidol and epichlorohydrin and the corrected values have been replotted in Figs. 4 and 5 to show the relative position of the nitrate ion to the other nucleophilic substances. As can be seen from the curves, the nitrate ion having a nucleophilic constant of 1.03 is the weakest nucleophilic substance measured thus far. Its perfect coincidence on the curves adds further support to the correlation of Swain and Scott.

Prediction of Yield Data.—In the synthesis[5] of several nitric esters by the addition of nitrate ion in aqueous solution, it was noted that a simple approximate relation of the type in the following equation was shown to apply under a fairly wide variety of conditions

$$\frac{n}{g} = r\frac{N_0}{W_0} \qquad (10)$$

As a result of the present kinetic study it is possible to derive this relation and to discuss in a somewhat quantitative manner the degree of the approximation for the oxides studied. Division of the rate expressions for the acid-catalyzed formation of nitric ester reaction D and glycol reaction B gives rise to the equation[12]

$$\frac{dn}{dg} = r\frac{(N_0 - n)}{(W_0 - g)} \qquad (11)$$

where symbols have been defined previously.

Integration of equation 11 gives

$$\left(\frac{N_0 - n}{N_0}\right)^{1/r} = \left(\frac{W_0 - g}{W_0}\right) \qquad (12)$$

Expanding the left-hand side of equation 12 by the binomial expansion and neglecting all powers higher than the first produces equation 10. An alternate derivation is to assume that in equation 11 $N_0 >> n$ and $W_0 >> g$ with subsequent integration. Both derivations are valid only when k_4/k_2 is constant. The kinetic data show that at high salt concentrations this constancy is ap-

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(10) C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

(11) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(12) In the kinetic derivations it is assumed that conditions are such that reactions A to D are essentially irreversible.

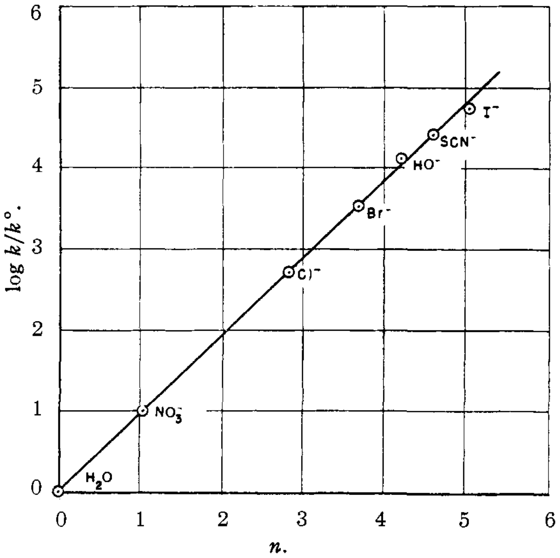


Fig. 4.—Rate correlation curve for glycidol.

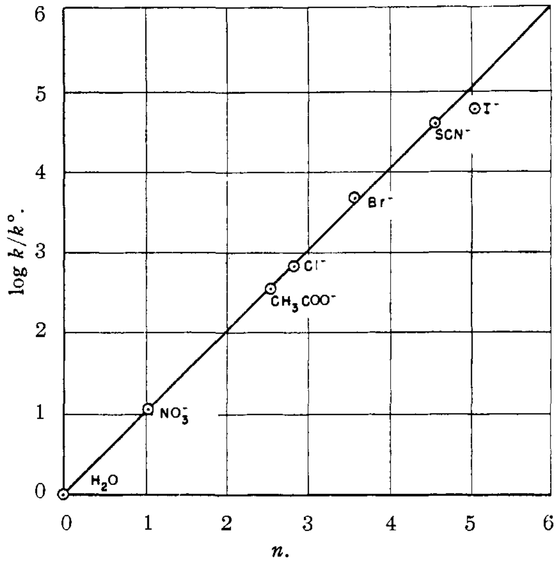


Fig. 5.—Rate correlation curve for epichlorohydrin.

proximately true, but at low concentrations equation 10 is far from valid. By retaining the quadratic term it can be shown that at higher oxide concentrations of E the ratio of n/N_0 to g/W_0 will be lower than r approximately by the fractional amount $E(r - 1)/(rN_0 + W_0)$. Therefore, under conditions of synthesis as described previously,[5] equation 10 can be expected to hold reasonably well in solutions as high as 5 and 6 molar.

PASADENA, CALIF.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF IOWA STATE COLLEGE AND HARVARD UNIVERSITY]

Some Halogen-Metal Interconversion Reactions with Methylphenyl Halides[1]

BY SANDERS D. ROSENBERG[2]

RECEIVED MARCH 26, 1954

A series of halogen-metal interconversion reactions have been run between phenyllithium and some methylphenyl halides. From the results of these, and several other interconversions reported, a series of relative electronegativities has been worked out; phenyl > o-tolyl > 2,4-dimethylphenyl > 2,6-dimethylphenyl, mesityl > butyl. Interconversion of p-bromobenzyl bromide with n-butyllithium yielded 1-amyl-4-bromobenzene and p-bromo-α-(p-bromomethylphenyl)-toluene.

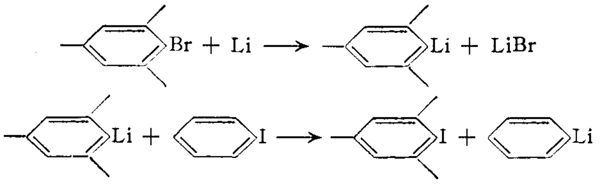
It has been postulated that the position of equilibrium in a halogen-metal interconversion reaction largely depends upon the relative electronegativities of the groups R and R′. When R and R′ have

$$RX + R'Li \rightleftarrows RLi + R'X$$

approximately the same electronegativity, the equilibrium mixture contains about equal amounts of the four compounds involved.[3] This idea has been supported by the halogen-metal interconversion of iodobenzene with p-tolyllithium followed by carbonation to yield benzoic acid (47%) and interconversion of p-iodotoluene with phenyllithium to give p-toluic acid (34%).[4] A study was undertaken to measure the changes in the position of equilibrium as more methyl groups were substituted on the benzene ring.

o-Iodotoluene was subjected to halogen-metal interconversion with phenyllithium to yield, on carbonation, o-toluic acid (15%). Phenyllithium and 2,4-dimethyliodobenzene gave 2,4-dimethylbenzoic acid (8%). Reactions between phenyllithium and 2,6-dimethyliodobenzene, bromomesitylene and iodomesitylene, respectively, gave no halogen-metal interconversions.

Conversely, interconversion of iodobenzene with 2,6-dimethylphenyllithium yielded benzoic acid (63%) and 2,6-dimethyliodobenzene (70%). Iodobenzene with mesityllithium gave benzoic acid (39%) and iodomesitylene (69%). The latter reaction offers a method for the preparation of iodomesitylene from bromomesitylene which gives a much better yield than the direct iodination of mesitylene.[5]



As it has been observed that the lithium atom tends to become attached to the more electronega-

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[1] Part of this research was supported by the Rubber and Plastics Branch, Wright Air Development Center.

[2] Research Laboratory, Metal & Thermit Corp., Rahway, N. J.

[3] "Organic Reactions," Vol. VI, 1951, p. 339.

[4] H. Gilman and R. G. Jones, THIS JOURNAL, 63, 1441 (1941).

[5] R. L. Datta and N. R. Chatterjee, *ibid.*, 39, 438 (1917).