account for the low yields of polystyrene found in several of the experiments (Table III). The residual polystyrene and residual catalyst were dissolved in benzene and precipitated by methanol. This process was repeated twice more and the polystyrene finally obtained as a brittle porous mass by the vacuum sublimation of benzene from a frozen benzene solution of the polymer.

Silanes as Co-catalysts.—In the preceding papers the rate of disproportionation of ethyltrimethylsilane, bromotrimethylsilane, trimethylsilane and phenyltrimethylsilane in cyclohexane solution and in the presence of aluminum bromide were reported.[2] The solvent also was examined by g.l.c. for isomerization during these disproportions. In no case was any appreciable isomerization of the cyclohexane to methylcyclopentane observed (see Table IV).

Acknowledgment.—The Vapor Fractometers were operated by Dr. E. Winslow and Mr. E. M. Hadsell; Mr. D. McBournie provided technical assistance for some of this work.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION]

Mechanism of Isocyanate Reactions with Ethanol[1]

BY L. L. FERSTANDIG AND ROBERT A. SCHERRER

RECEIVED MARCH 26, 1959

The rates of reaction with ethanol of a group of phenyl-substituted isocyanates (phenyl isocyanate, *m*-tolylene diisocyanate and *p,p'*-diisocyanatodiphenylmethane) and a group of benzyl-substituted isocyanates (benzyl isocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate and 5-*t*-butyl-1,3-xylylene diisocyanate) were measured and compared. The energies of activation were calculated using the Arrhenius equation. The benzyl type reacts more slowly than the phenyl type, but their rates converge at higher temperatures because the former have significantly higher energies of activation. The reaction mechanism, which is the same for both classes, is first order in isocyanate and in alcohol concentration. The observation that electron-withdrawing substituents accelerate the rate of reaction is discussed with respect to the fine mechanism of the reaction.

In recent years, a new type of polyester rubber[2] has been developed which requires the use of diisocyanates. In this synthesis, the reaction of hydroxyl groups with isocyanate groups is quite important. We chose this reaction for study in order to compare several new diisocyanates with previously available diisocyanates.

There are several publications in the literature on the rate of reaction of phenyl isocyanates with alcohols.[3-9] There are also papers on the rate of reaction of substituted-phenyl isocyanates with alcohol[10,11] in the presence of amine catalysts. However, there have been no papers published comparing the reactivity of phenyl and benzyl isocyanates.

Experimental

Synthesis.—The isocyanates which could not be obtained commercially were synthesized by the method of Siefken[12]

$$RNH_2 \cdot HCl + COCl_2 \longrightarrow RNCO + 3HCl$$

The apparatus consisted of a 500-ml. baffled cylindrical flask provided with vigorous stirring, a gas inlet tube, a thermocouple well, and an air condenser which was attached to a gas scrubber containing 25% alkali to remove hydrogen chloride and phosgene from the off-gases. The flask was wrapped with a tape heating element. Facilities for switching from phosgene to nitrogen were provided at the inlet tube so that the system could be freed of phosgene before it was opened.

The solid amine hydrochloride was stirred and heated in *o*-dichlorobenzene, under nitrogen, until the solvent reached its boiling point. Phosgene then was passed in until all the hydrochloride reacted as noted by the change from an inhomogeneous to a homogeneous solution. The reaction mixture was freed of solvent at 115° (100 mm.) and the residue was distilled through a two-plate column. The reaction data and yields are given in Table I.

Rate Studies.—The reactions were run in a stoppered, 100-ml. graduated cylinder under a nitrogen atmosphere, using freshly distilled isocyanates, absolute ethanol and reagent grade toluene. An example follows (typical data are plotted in Fig. 1).

Eighty-five milliliters (72.4 g.) of toluene was measured into the graduated cylinder. The cylinder was stoppered and placed in the thermostat at 30.00° (±0.05°) or 40.00° and allowed to come to temperature equilibrium for one-half hour. Similarly, 15 ml. (12.2 g.) of absolute ethanol was measured into a tared, stoppered, 25-ml. graduate and allowed to come to temperature equilibrium. Sufficient isocyanate was added to the toluene to yield approximately 0.1 *N* isocyanate in the final solution. The ethanol was poured into the toluene solution at zero time. The exact weight of ethanol added was determined by the difference in the initial and final weights of the 25-ml. graduate. Two-milliliter samples, which were withdrawn while maintaining a stream of nitrogen over the open cylinder, were taken at intervals varying from 30 seconds to 30 minutes. The samples were drained into 10-ml. aliquots of approximately 0.04 *N* dibutylamine in toluene. The isocyanate sample was permitted to stand with the dibutylamine for five minutes, then 150 ml. of methanol and 1 ml. of brom phenol blue indicator solution were added. The excess dibutylamine was titrated with 0.01 *N* hydrochloric acid. This titer was subtracted from the titer of a 10-ml. aliquot of dibutylamine solution, the difference being the isocyanate normality. The analytical procedure was checked with known amounts of each isocyanate used and was shown to be reproducible within the overall experimental error. It also was demonstrated that the dibutylamine reacted with the isocyanate quantitatively in less than one minute. Thus, the amine solution was an effective shortstop.

Discussion and Results

The study by Baker and Gaunt[4] indicates that the probable mechanism of reaction of phenyl isocyanate and alcohols follows the path

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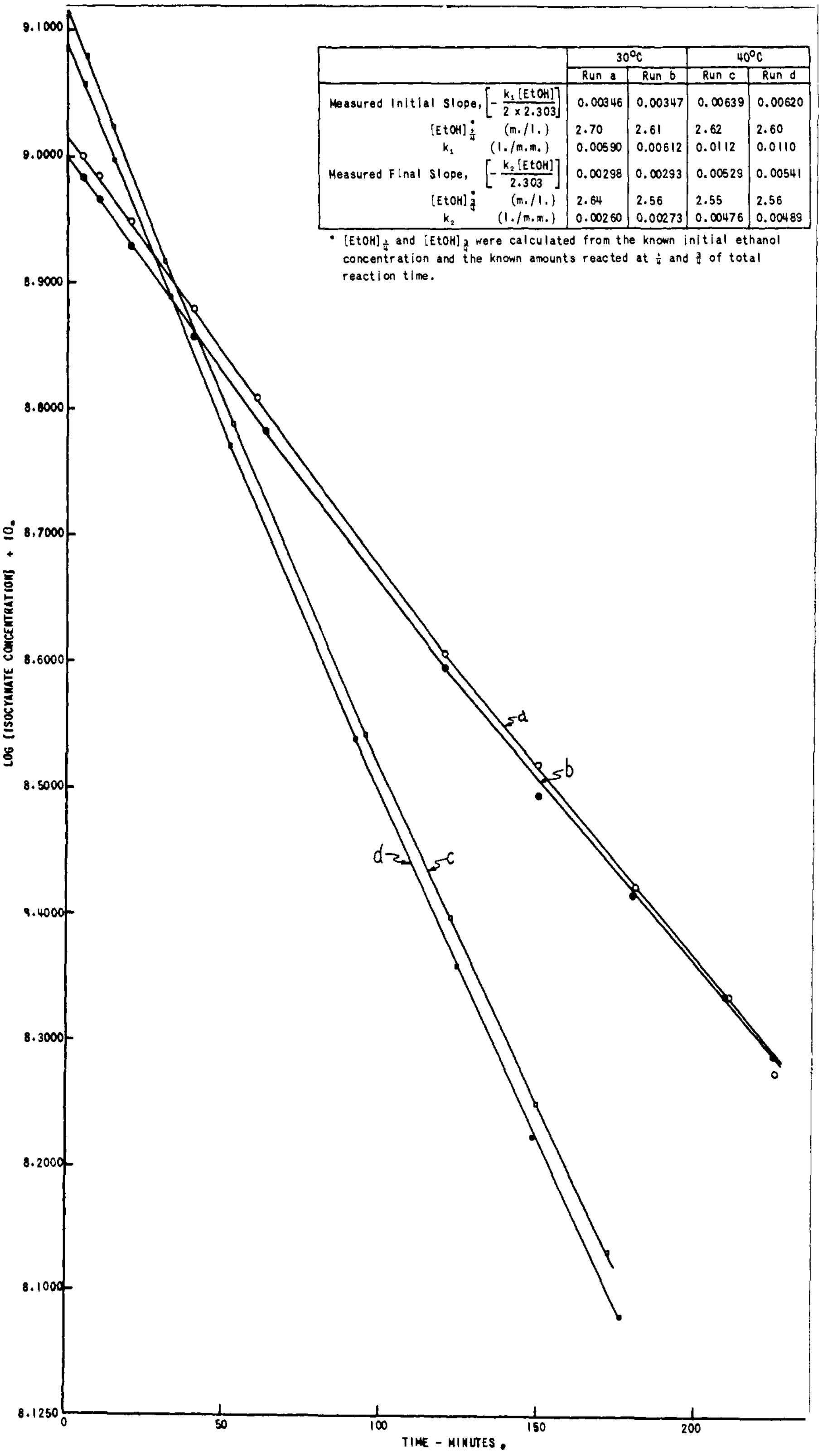


	30°C		40°C	
	Run a	Run b	Run c	Run d
Measured Initial Slope, $\left[-\frac{k_1[\mathrm{EtOH}]}{2 \times 2.303}\right]$	0.00346	0.00347	0.00639	0.00620
$[\mathrm{EtOH}]^{*}_{\frac{1}{4}}$ (m./l.)	2.70	2.61	2.62	2.60
k_1 (l./m.m.)	0.00590	0.00612	0.0112	0.0110
Measured Final Slope, $\left[-\frac{k_2[\mathrm{EtOH}]}{2.303}\right]$	0.00298	0.00293	0.00529	0.00541
$[\mathrm{EtOH}]^{*}_{\frac{3}{4}}$ (m./l.)	2.64	2.56	2.55	2.56
k_2 (l./m.m.)	0.00260	0.00273	0.00476	0.00489

* $[\mathrm{EtOH}]_{\frac{1}{4}}$ and $[\mathrm{EtOH}]_{\frac{3}{4}}$ were calculated from the known initial ethanol concentration and the known amounts reacted at $\frac{1}{4}$ and $\frac{3}{4}$ of total reaction time.

Fig. 1.—Typical duplicate experimental curves; *m*-xylylene diisocyanate.

$$\mathrm{PhNCO} + \mathrm{ROH} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\mathrm{ROH}}{\underset{\vdots}{\mathrm{PhNCO}}} \text{ (complex)} \qquad \text{(I)}$$

$$\text{Complex} + \mathrm{ROH} \xrightarrow{k_3} \mathrm{PhNHCO_2R} + \mathrm{ROH} \qquad \text{(II)}$$

Assuming a steady state concentration of the com-

TABLE I

ISOCYANATE SYNTHESIS AND BOILING POINT DATA

Compound	Mole of amine hydrochloride per 200 ml. of *o*-dichlorobenzene	Temp. of reacn., °C.	Time of reacn., hr.	Yield of pure products, mole %	B.p. °C.	B.p. Mm.	M.p., °C.
Benzyl isocyanate	0.200	130	3.0	88.0	137	30	
1,3-Xylylene diisocyanate	.152	182	13.0	81.4	130	2	
1,4-Xylylene diisocyanate	.172	180	11.0	77.0	138	2.2	46.5
5-*t*-Butyl-1,3-xylylene diisocyanate	.093	180	8.8	94.2	159	2	
Phenyl isocyanate					161	760	
m-Tolylene diisocyanate					118	10	
p,p'-Diisocyanatodiphenylmethane					150	0.3	37.5
α-Naphthyl isocyanate					110	3.5	
1,5-Naphthalene diisocyanate					131	0.2	~130

plex, then the rate of product formation is

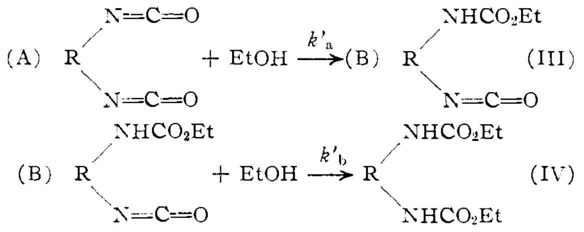
$$\text{rate} = \frac{k_1\, k_3}{k_2/[\text{ROH}] + k_3}\,[\text{PhNCO}][\text{ROH}]$$

The conditions chosen for this work do not provide a good test for the Baker and Gaunt mechanism, for in order to simplify the experimental technique the reactions were swamped with ethanol. This results in a pseudo first-order reaction dependent only upon isocyanate concentration. Using this flooding technique, it is not possible to determine whether the order of ethanol reaction is simple first order or complicated as above. Actually, at high ethanol-to-isocyanate ratios, k_2[ROH] is negligible with respect to k_3 so that the reaction may be considered first order in alcohol and first order in isocyanate, permitting a simplified approach which facilitates the mathematics for the difunctional studies, *i.e.*[13]

$$k_{\text{exp}} = \frac{k_1 k_3}{k_2/[\text{ROH}] + k_3} \cong k_1$$

This, of course, implies that reaction I is slow and reaction II is fast. The data, insofar as they do overlap, are in excellent agreement with Baker and Gaunt with respect both to the specific over-all rate constants and to the energies of activation.

Using the simplified treatment for the determination of the two rate constants in difunctional cases, the reactions are written ignoring the fast step



The difunctional isocyanate may be called A and the half reacted isocyanate, B. The differential equations for reactions III and IV are

$$dA/dt = -k_a'[\text{EtOH}][\text{A}] \text{ and}$$
$$dB/dt = k_a'[\text{EtOH}][\text{A}] - k_b'[\text{EtOH}][\text{B}]$$

and since [EtOH] is constant, we may define

$$k_a'[\text{EtOH}] = k_a \text{ and } k_b'[\text{EtOH}] = k_b$$

The integrated equations are

$$A = A_0 e^{-k_a t} \text{ and } B = A_0 \frac{k_a}{k_b - k_a}\left(e^{-k_a t} - e^{-k_b t}\right)$$

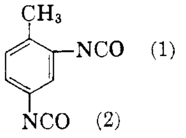
The analytical determination of isocyanate groups does not distinguish between A and B nor between mono- and difunctionality. Thus, the concentration of NCO groups [C] equals $2A$ plus B or more generally

$$C = n_1 A + n_2 B$$

Given a set of [C] *versus* time values, this equation was solved with the aid of a digital computer (Datatron) by a program which calculates a set of values for k_a, k_b and A_0 using the criterion of least squares, *viz.*, such that $\Sigma(C_{\text{table}} - C_{\text{computed}})^2$ is a minimum, the sum being taken over all values. The special case of $n_1 = 1$ and $n_2 = 0$ was used for monofunctional reactions. Data calculated by this method are given in Tables II and III.

An approximate mathematical approach can also be used with a fair degree of success. In this method the assumption that the concentration of B is negligible near the beginning of the reaction and similarly that the concentration of A is negligible near the end of the reaction was used. In this way the differential equations involving A and B can be integrated readily. This treatment predicts that the over-all curve for log [NCO] *versus* time should be two straight lines joined by a curved portion in the middle (where neither A nor B is negligible and the above treatment is not applicable). The experimental curves for this treatment are shown in Figs. 1 and 2. Also shown in Fig. 1 is a table giving the first and second rate constants for *m*-xylylene diisocyanate calculated using the approximate method.

The determination of the two rate constants for diisocyanates where the two isocyanate groups are equivalent is, therefore, experimentally practical. In the case where the two isocyanate groups are not equivalent, *i.e.*, *m*-tolylene diisocyanate, the



two rate constants have been resolved only approximately because at the beginning of the reac-

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(13) In order to check this assumption, we used the data of Baker and Gaunt on the value of the ratio k_3/k_2 since

$$\frac{k_1 k_3}{k_2/[\text{ROH}] + k_3} = k_1\left(\frac{1}{\dfrac{k_2}{k_3[\text{ROH}]} + 1}\right)$$

With $k_3/k_2 = 2.27$ (p. 28 in ref. 3) and our alcohol concentration of 2.61 m./l., the coefficient becomes 0.85 k_1.

TABLE II

RATE DATA FOR ISOCYANATES WITH EXCESS ETHANOL IN TOLUENE

Compound	T, °C. ($\pm 0.05°$)	$k_a \times 10^2$ Liters/mole min.	$k_a \times 10^2$ Average	$k_b \times 10^2$ Liters/mole min.	$k_b \times 10^2$ Average
Phenyl isocyanate	30	3.13, 3.06	3.09		
	40	5.03, 5.17	5.10		
m-Tolylene diisocyanate[a]	30	9.4	9.4	0.39	0.39
	40	17.5, 18.9	16.6	0.76, 0.81	0.78
p,p'-Diisocyanatodiphenylmethane	30	6.92, 7.30	7.11	2.24, 2.24	2.24
	40	10.8, 10.0	10.4	3.54, 3.80	3.67
α-Naphthyl isocyanate	30	1.30, 1.29	1.29		
	40	2.06, 2.11	2.09		
1,5-Naphthalene diisocyanate	30	7.3, 9.5	8.4	2.2, 2.6	2.4
	40	10.6, 11.5	11.0	4.02, 3.78	3.90
Benzyl isocyanate	30	0.288, 0.320	0.304		
	40	0.445, 0.440	0.443		
1,3-Xylylene diisocyanate	30	0.622, 0.622	0.622	0.260, 0.252	0.255
	40	1.24, 1.18	1.21	.483, .473	.478
1,4-Xylylene diisocyanate	30	0.563, 0.569	0.566	.322, .243	.283
	40	1.32, 1.18	1.25	.396, .484	.439
5-*t*-Butyl-1,3-xylylene diisocyanate	30	0.600, 0.618	0.609	.225, .220	.223
	40	1.17, 1.10	1.14	.423, .414	.419

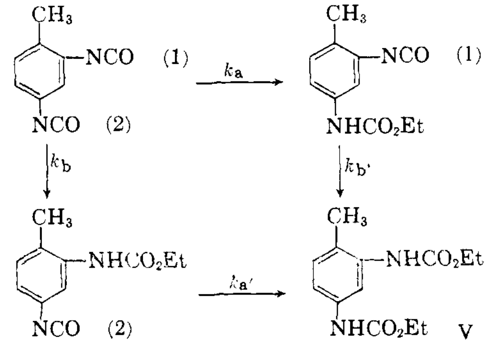
[a] The numbers appearing under columns k_a and k_b represent $k_a + k_b$ and k_b', respectively, for *m*-tolylene diisocyanate (see text).

TABLE III

RELATIVE RATES AT 30° AND ENERGIES OF ACTIVATION

Compound	k_a	k_b	E_{act}, kcal. k_a	E_{act}, kcal. k_b
Phenyl isocyanate	14		9.5	
m-Tolylene diisocyanate	42	1.7	11	
p,p'-Diisocyanatodiphenylmethane	32	10	7.2	9.4
α-Naphthyl isocyanate	5.8		9.1	
1,5-Naphthalene diisocyanate	38	11	5.1	9.3
Benzyl isocyanate	1.4		7.2	
1,3-Xylylene diisocyanate	2.8	1.1	12.6	11.9
1,4-Xylylene diisocyanate	2.5	1.3	13.9	11.2
5-*t*-Butyl-1,3-xylylene diisocyanate	2.7	1.0	11.8	11.9

tion, both groups (1) and (2) are reacting (V), and a combined rate is obtained. Toward the end, however, the rate constant (k_b') for the slowest of the four reactions[14] can be determined accurately.



V

The data are given for *m*-tolylene diisocyanate as $k_a + k_b$ and k_b'. However, k_b' and k_b should be about the same since the reaction is occurring at the same site (NCO group 1), and the only difference between k_b and k_b' is the effect of the *meta* substituent. Neglecting this effect, k_b' may be subtracted from $k_a + k_b$ to give an approximate value of k_a.

The data for all the kinetics runs are given in Table II. Relative rates at 30° are shown in Table III. Also given are approximate energies of activation calculated by the Arrhenius equation from data at 30 and 40°.

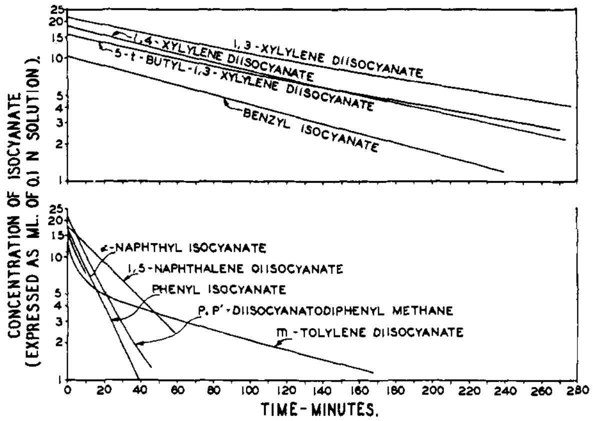


Fig. 2.—Rate of reaction of isocyanates with ethanol at 30°.

From these data the isocyanate and urethan substituents can be compared to hydrogen in their effects on the rate simply by comparing the k_a and k_b to the k for the unsubstituted isocyanate (phenyl or benzyl). The data for both the phenyl and benzyl types show that the electron-withdrawing isocyanate substituent increases the rate, and the electron-releasing urethan substituent decreases the rate relative to hydrogen as a substituent. These effects can be explained by assuming that the reaction depends upon the electrophilic character of the isocyanate carbon; *i.e.*, electron-withdrawing groups make the isocyanate carbon more electrophilic (positive) and thus increase the rate of reaction with nucleophilic alcohol.[8]

The benzyl type of isocyanate is much slower to react than the phenyl type, but this is not surprising

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(14) D. M. Simons and R. C. Arnold, THIS JOURNAL, **78**, 1658 (1956).

since the isocyanate groups are insulated from the electron-withdrawing benzene ring in the former type. It is surprising that the substituent effects are of the same order of magnitude for both the phenyl and benzyl types. Also, the benzyl type does have a higher energy of activation than the phenyl type. The extrapolation using the Arrhenius equation shows that the rates converge for the two classes at about 170°.

It is interesting to note that the isocyanate group *ortho* to the methyl group in *m*-tolylene diisocyanate is severely hindered in rate. However, the *meta t*-butyl group in 5-*t*-butyl-1,3-xylylene diisocyanate does not cause an appreciable change in the rate of reaction of either of its neighboring isocyanate groups compared to unsubstituted 1,3-xylylene diisocyanates.

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RICHMOND, CALIF.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

Carbanions. II. Cleavage of Tetraalkylammonium Halides by Sodium in Dioxane[1,2]

BY ERLING GROVENSTEIN, JR., ELWOOD P. BLANCHARD, JR., DAVID A. GORDON AND ROBERT W. STEVENSON

RECEIVED JANUARY 28, 1959

Quaternary ammonium salts react with sodium in boiling dioxane to give alkane and tertiary amine by reductive cleavage and olefin and tertiary amine by an accompanying Hofmann-type elimination. Tetramethylammonium halides, in addition to methane and trimethylamine, give small amounts of ethylene and ethyldimethylamine. Ethylene is also a minor component of the olefins produced from other quaternary ammonium halides having at least one N-methyl group. Cleavage of salts of the type $R_n(CH_3)_{4-n}NX$ permits measurement of the relative amounts of RH and CH_4 produced. The ratio of RH to CH_4 obtained, after statistical correction for unequal numbers of groups and multiplication by 100, is: *n*-Pr, 2.4 ± 0.3; *n*-Bu, 2.6 ± 0.7; Et, 4.2 ± 0.5; *i*-Pr, 28.2 ± 1.9; *s*-Bu, 53 ± 3; Me, 100; allyl, 1050 ± 120; *t*-Bu, 10,800 ± 1000. Similar reductive cleavages of quaternary ammonium salts can be obtained in dioxane-*t*-amyl alcohol mixture and in cumene. Dioxane is not appreciably cleaved by sodium but is cleaved by sodium-potassium alloy to give ethylene and some ethylene glycol. Methyl *t*-butyl ether was not appreciably cleaved under any of the conditions tried with sodium and sodium-potassium alloy.

The reductive cleavage of quaternary ammonium salts to hydrocarbon and tertiary amine by reaction with an excess of sodium amalgam in aqueous or aqueous alcoholic medium is known as the Emde degradation. An example[3] is

$$C_6H_5CH{=}CHCH_2N(CH_3)_3Cl + 2Na + H_2O \longrightarrow C_6H_5CH{=}CHCH_3 + N(CH_3)_3 + NaCl + NaOH$$

The ease of cleavage of groups as hydrocarbon component is $R\overset{\overset{O}{\|}}{C}CH_2$, $C_6H_5CH{=}CHCH_2 > C_6H_5CH_2 > CH_2{=}CHCH_2 > C_6H_5 \geq CH_3$ as judged by competitive cleavage of groups from quaternary ammonium cations containing two or more such groups.[4] Such an order of relative reactivity might be expected if either a carbanion or a free radical were produced as reactive intermediate in the product-determining stage of the reaction.

It occurred to us that for saturated alkyl groups carbanion and free radical stability are affected in different ways by alkyl substitution at the trivalent carbon atom and, therefore, that a study of the relative ease of cleavage of saturated alkyl groups might provide information concerning the nature of the Emde degradation. A practical difficulty to such a study, however, is the report of Emde and coworkers that ammonium compounds with four saturated alkyl groups are not cleaved by sodium amalgam. Thus Emde and Kull[4g] reported that N,N-dimethylpiperidinium chloride is not cleaved and similar results were obtained for methyldiethyl-β-hydroxyethylammonium chloride[5] and related compounds.[6] Methyl cleavage, however, has been observed in some cases. Thus v. Braun and Aust[4c] reported that 40% of the tertiary amine from reaction of N,N-dimethyltetrahydroquinolinium chloride with sodium amalgam was N-methyltetrahydroquinoline. Although methane would be expected as a corresponding product from this reaction, Emde and Kull[4g] have suggested, without citing evidence, that methyl alcohol is produced instead. Groenewoud and Robinson[4h] in their study of cleavage of aryltrimethylammonium chloride by sodium amalgam obtained 5 to 80% of aryldimethylamine, depending upon the aryl group. These authors did not identify the fate of the methyl group in their cleavages; however they did show that their quaternary ammonium chlorides were unreactive toward sodium hydroxide under conditions which were rather similar to those employed in their reactions with sodium amalgam. It accordingly seems probable, as they suggested, that the methyl group appeared as

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(1) More extensive experimental details are recorded in theses at the Georgia Institute of Technology: D. A. Gordon, Ph.D. thesis, June, 1953; E. P. Blanchard, Jr., M.S. thesis, June, 1954; R. W. Stevenson, Ph.D. thesis, May, 1958.

(2) Paper I in this series is considered to be that of E. Grovenstein, Jr., THIS JOURNAL, **79**, 4985 (1957).

(3) H. Emde, *Arch. Pharm.*, **244**, 289 (1906).

(4) (a) H. Emde, *ibid.*, **247**, 369 (1909); **249**, 106 (1911); (b) H. Emde and P. Schellbach, *ibid.*, **249**, 118 (1911); (c) J. v. Braun and E. Aust, *Ber.*, **49**, 501 (1916); (d) J. v. Braun and L. Neumann, *ibid.*, **50**, 50 (1917); (e) J. v. Braun, J. Seemann and A. Schultheiss, *ibid.*, **55**, 3803 (1922); (f) T. S. Stevens, E. M. Creighton, A. B. Gordon and M. MacNicol, *J. Chem. Soc.*, 3193 (1928); (g) H. Emde and H. Kull, *Arch. Pharm.*, **272**, 469 (1934); (h) P. Groenewoud and R. Robinson, *J. Chem. Soc.*, 1692 (1934).

(5) H. Emde and A. Runne, *Arch. Pharm.*, **249**, 371 (1911).

(6) H. Emde, *Helv. Chim. Acta*, **15**, 1330 (1932).