On the Mechanism of the Electrolytic Reduction of the Carbon–Halogen Bond. II. A $\rho\sigma$ Study[1]

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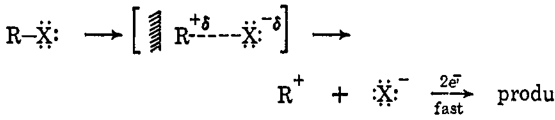
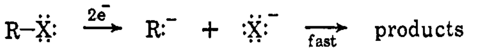
Abstract: Plots of polarographic half-wave potentials in dimethylformamide and acetonitrile *vs.* σ for substituted chlorobenzenes, bromobenzenes, iodobenzenes, and benzyl bromides indicate a negatively charged potential-determining transition state. These and similar results by others rule out an SN1-type mechanism.

Of the several distinct pathways which have been proposed for the electrochemical reduction of the carbon–halogen bond only one, the SN1 mechanism I,[2–4] requires that the carbon acquire a positive charge in the potential-determining state. This charge results



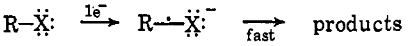
$$\mathrm{R{-}\ddot{\underset{..}{X}}\!:} \longrightarrow \left[\mathrm{R}^{+\delta}\text{----}\ddot{\underset{..}{\mathrm{X}}}\!:^{-\delta} \right] \longrightarrow \mathrm{R}^{+} + :\ddot{\underset{..}{\mathrm{X}}}\!:^{-} \xrightarrow[\text{fast}]{2e^{-}} \text{products} \qquad \text{(I)}$$

from the breaking of the carbon–halogen bond by the intense electric field very close to the electrode surface before electron transfer from the electrode occurs. By contrast, all of the other proposed mechanisms—carbanion (II),[2,3,5] free radical (III),[2,3] and radical anion (IV)[6–9]—propose the uptake of one or two electrons in the potential-determining step. Mechanism IV would



$$\mathrm{R{-}\ddot{\underset{..}{X}}\!:} \xrightarrow{2e^{-}} \mathrm{R}\!:^{-} + :\ddot{\underset{..}{\mathrm{X}}}\!:^{-} \xrightarrow[\text{fast}]{} \text{products} \qquad \text{(II)}$$

$$\mathrm{R{-}\ddot{\underset{..}{X}}\!:} \xrightarrow{1e^{-}} \mathrm{R}\cdot + :\ddot{\underset{..}{\mathrm{X}}}\!:^{-} \xrightarrow[\text{fast}]{} \text{products} \qquad \text{(III)}$$



$$\mathrm{R{-}\ddot{\underset{..}{X}}\!:} \xrightarrow{1e^{-}} \mathrm{R}\overset{\cdot}{-}\ddot{\underset{..}{\mathrm{X}}}\!:^{-} \xrightarrow[\text{fast}]{} \text{products} \qquad \text{(IV)}$$

obviously have a negatively charged carbon atom in the transition state. Mechanisms II and III would also have negative carbon, unless the halide ion departure were sufficiently rapid to equal or exceed the rate of electron transfer from the cathode. Elving, Markowitz, and Rosenthal[10] have pointed out that such situations can be considered as mixtures of simpler mechanisms and have suggested the name "ionic mechanism" for a blend of I and II which can vary with different substrates and experimental conditions.

The sign of the charge on carbon in the transition state can be determined if the Hammett linear free energy relationship holds for a plot of polarographic half-wave potential *vs.* σ for a series of substituted halides. Zuman[11] has summarized the theoretical justification for such a plot and has shown that the half-wave potentials for 11 iodobenzenes with substituents having σ values in the range -0.268 to $+0.227$ fall close to a straight line with positive ρ value. In a similar study with six benzyl bromides, Klopman,[12] using anhydrous methanol as the solvent and lithium methoxide or lithium chloride as the electrolyte, concluded that both electron-attracting and electron-releasing substituents facilitated reduction. Streitwieser and Perrin[8] have reported that half-wave potentials for a number of substituted benzyl chlorides polarographed in dimethylformamide containing tetraethylammonium chloride give only a rough approximation to a straight line, although the slope is undoubtedly positive. In similar work, Lambert[5b] has shown a linear correlation between the half-wave potentials of a considerable number of alkyl bromides and the corresponding Taft polar substituent constants (σ^*) and has pointed out that the slope of the line indicates a negatively charged transition state.

It is important to learn whether the behavior observed by Klopman with benzyl bromides also occurs in other systems or whether halogen reductions typically show linear free energy relationships with positive values for ρ. To this end, a number of substituted benzyl bromides, iodobenzenes, bromobenzenes, and chlorobenzenes have been polarographed; particular efforts have been made to get substituents which have larger positive and negative σ values than those previously studied. Dimethylformamide with tetraethylammonium bromide electrolyte was used for most of this work because its useful range extends to very negative potentials, but a considerable number of experiments were also run in acetonitrile.

Results

The half-wave potentials found in dimethylformamide and acetonitrile for benzyl bromide, iodobenzene, bromobenzene, and chlorobenzene derivatives are given in Table I. When a reducible substituent was present, the assignment of a half-wave potential to the carbon–

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(1) This article is based on theses submitted in partial fulfillment of the requirements for the M.A. degree of Wesleyan University by F. G. Burton in June 1966 and by S. L. Nickol in June 1965.

(2) P. J. Elving, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **14**, 99 (1953).

(3) P. J. Elving and B. Pullman, *Advan. Chem. Phys.*, 3, 1 (1961).

(4) F. L. Lambert, A. H. Albert, and J. P. Hardy, *J. Am. Chem. Soc.*, **86**, 3155 (1964).

(5) Carbanion is used instead of SN2 in describing the two-electron transfer to avoid any steric implications associated with the latter term; a feature of the original SN2 mechanism was the back-side attack by the electrode on the carbon of the carbon–halogen bond. This has since been found to be untenable. See (a) J. W. Sease, P. Chang, and J. L. Groth, *ibid.*, **86**, 3154 (1964); **87**, 5809 (1965); (b) F. L. Lambert, *J. Org. Chem.*, **31**, 4184 (1966); (c) R. Annino, R. E. Erickson, J. Michalovic, and B. McKay, *J. Am. Chem. Soc.*, **88**, 4424 (1966).

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(7) L. W. Marple, L. E. I. Hummelstedt, and L. B. Rogers, *J. Electrochem. Soc.*, 107, 437 (1960).

(8) A. Streitwieser, Jr., and C. Perrin, *J. Am. Chem. Soc.*, **86**, 4938 (1964).

(9) C. K. Mann, J. L. Webb, and H. M. Walborsky, *Tetrahedron Letters*, 20, 2249 (1966).

(10) P. J. Elving, J. M. Markowitz, and I. Rosenthal, *J. Electrochem. Soc.*, 101, 195 (1954).

(11) P. Zuman, *Collection Czech. Chem. Commun.*, **25**, 3225 (1960). See also P. J. Elving and J. M. Markowitz, *J. Org. Chem.*, **25**, 18 (1960).

(12) G. Klopman, *Helv. Chim. Acta*, **44**, 1908 (1961).

Table I. Half-Wave Potentials of Aryl and Benzyl Halides

	Substituent	σ^a	Substituted iodobenzenes[b]	Substituted bromobenzenes[b]	Substituted chlorobenzenes[b]	Substituted benzyl bromides[b]
1	m-NMe_3^+	0.88, 0.85[c]			−1.48 (−1.57)	
2	p-NMe_3^+	0.82, 0.75[c]	−0.91 (−0.94)	−1.34 (−1.41)		
3	p-CN	0.66, 1.018[d]		−1.26 (−1.37)	−1.36 (−1.48)	−0.42
4	m-CN	0.56, 0.653[d]		−1.29 (−1.41)		
5	p-CF_3	0.54	−1.01 (−1.02)	−1.53 (−1.61)		
6	p-COMe	0.502, 0.874[e]	−1.04 (−1.12)	−1.15 (−1.24)		
7	p-COC_6H_5	0.459,[g] 0.98[h]	−0.96 (−1.01)	−1.06 (−1.13)		
8	m-CF_3	0.43	−1.00 (−1.02)	−1.52 (−1.59)		
9	m-Br	0.391	−0.96 (−0.98)	−1.45 (−1.50)		−0.62
10	m-COMe	0.376, 0.99[f]		−1.19 (−1.29)		
11	m-Cl	0.373	−0.98 (−1.00)	−1.53 (−1.59)		−0.71
12	m-I	0.352	−0.92 (−0.96)			
13	m-F	0.337				−0.71
14	p-I	0.276[e]	−1.01 (−1.03)			
15	p-Br	0.232	−1.08 (−1.10)	−1.54 (−1.62)		−0.72
16	p-Cl	0.227	−1.06 (−1.08)	−1.61 (−1.72)	−1.85 (−2.05)	−0.73
17	p-CHO	0.216,[g] 1.126[g]	−0.96 (−1.01)		−1.20 (−1.26)	
18	m-OMe	0.115	−1.19 (−1.23)	−1.76 (−1.84)		−0.80
19	p-F	0.062				−0.84
20	m-C_6H_5	0.06	−1.15 (−1.16)	−1.58 (−1.73)		
21	β-C_4H_4[i]	0.042, 0.120[d]	−1.16 (−1.17)	−1.47 (−1.61)		
22	p-NHCOMe	0.00		−1.88 (−1.83)	−2.09 (−2.16)	
23	H	0.00	−1.21 (−1.23)	−1.81 (−1.91)	−2.13	−0.82
24	p-C_6H_5	−0.01	−1.16 (−1.20)	−1.56 (−1.70)		
25	m-Me	−0.069	−1.22 (−1.24)	−1.85 (−1.95)	−2.16	−0.78
26	p-Me	−0.170	−1.23 (−1.26)	−1.84 (−1.96)	−2.16	−0.80
27	m-NMe_2	−0.211			−2.23	
28	p-OEt	−0.24		−1.82 (−1.93)		
29	p-OMe	−0.268	−1.25 (−1.26)	−1.84 (−1.95)	−2.15	−0.87
30	p-OC_6H_5	−0.320, 0.028[g]		−1.73 (−1.81)		
31	p-NMe_2	−0.60, −0.44[h]	−1.35 (−1.36)	−1.97 (−2.04)		
32	p-NH_2	−0.66, −0.38[h]		−1.96 (−2.07)		

[a] Where σ^- values are available, they are given after the conventional σ value. Unless specified otherwise, values were taken from D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958). [b] Half-wave potentials in parentheses refer to acetonitrile solution; other values were obtained in dimethylformamide solution. All potentials are in volts *vs.* a Ag | AgBr anode in 0.02 *M* Et_4NBr and are corrected for *iR* drop in cell. [c] J. D. Roberts, R. A. Clement, and J. J. Drysdale, *J. Am. Chem. Soc.*, **73**, 2181 (1951). [d] M. M. Fickling, A. Fischer, B. R. Mann, J. Packer, and J. Vaughan, *ibid.*, **81**, 4226 (1959). [e] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940. [f] J. H. Vandenbelt, C. Henrich, and S. G. Vandenberg, *Anal. Chem.*, **26**, 726 (1954). [g] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). [h] L. K. Dyall, *Australian J. Chem.*, **17**, 419 (1964). [i] The test substance was 2-bromonaphthalene.

halogen reduction step was made by comparing the waves of the reduction curve of the halogen-free compound (benzaldehyde, acetophenone, benzophenone, or benzonitrile) with those of the substituted halogen compounds. The plots of dimethylformamide values in Figures 1–4 show that, despite some scatter, the data can be fitted reasonably well to straight lines which have clearly positive slopes in every case. For chlorobenzene and bromobenzene derivatives, whose plots had the steepest positive slopes, the use of σ^- values obtained from aniline systems, when available, gave considerably less scatter than the conventional σ values based on benzoic acid dissociation constants. Either set of σ values gave an equally good fit in plotting the iodobenzene and benzyl bromide values, where the slope was considerably less positive than in the other

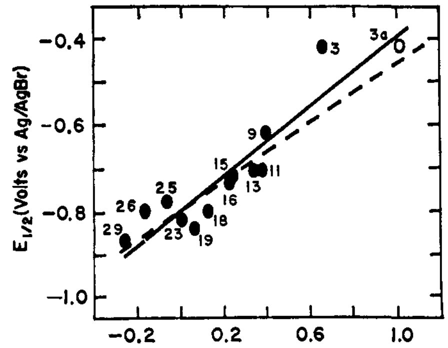

Figure 1. $E_{1/2}$-σ plot for benzyl bromides: ●, σ; ———, $E_{1/2} = -0.80 + 0.40\sigma$, δ 0.06 for 12 points. ○, σ^-; – – – –, $E_{1/2} = -0.80 + 0.34\sigma^-$ (σ used when σ^- not available), δ 0.04 for 12 points.

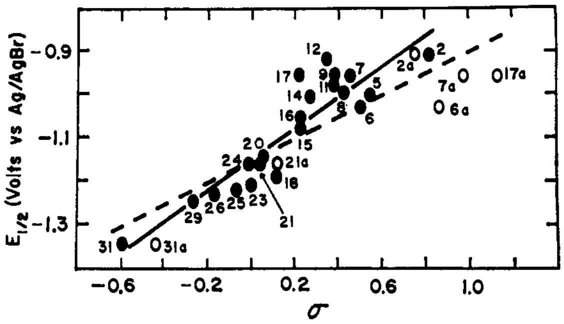

Figure 2. $E_{1/2}$-σ plot for iodobenzenes: ●, σ; ———, $E_{1/2} = -1.15 + 0.35\sigma$, δ 0.05 for 21 points. ○, σ^-; – – – –, $E_{1/2} = -1.16 + 0.26\sigma^-$ (σ used when σ^- not available), δ 0.07 for 21 points.

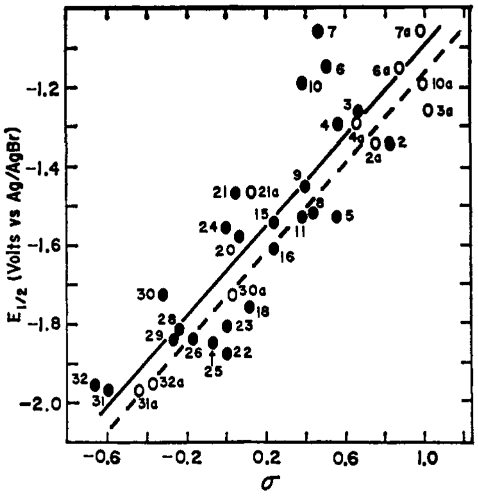

Figure 3. $E_{1/2}$–σ plot for bromobenzenes: ●, σ; ———, $E_{1/2} = -1.66 + 0.57\sigma$, δ 0.15 for 25 points. ○, σ^-; – – – –, $E_{1/2} = -1.72 + 0.56\sigma^-$ (σ used when σ^- not available), δ 0.09 for 25 points.

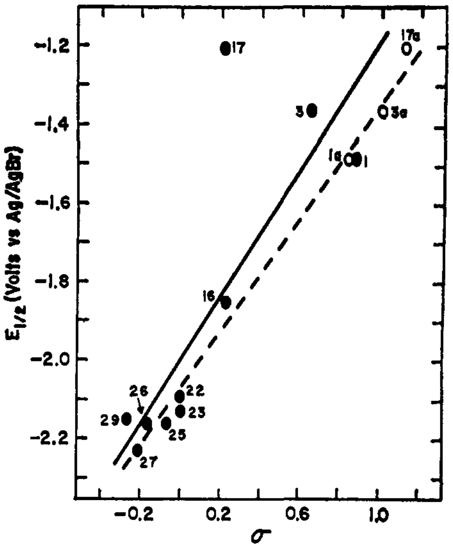

Figure 4. $E_{1/2}$–σ plot for chlorobenzenes: ●, σ; ———, $E_{1/2} = -1.99 + 0.81\sigma$, δ 0.25 for 10 points. ○, σ^-; – – – –, $E_{1/2} = -2.06 + 0.71\sigma^-$ (σ used when σ^- not available), δ 0.06 for 10 points.

two cases. The *p*-OMe derivative of benzyl bromide has a noticeably more negative half-wave potential than benzyl bromide itself, thus making highly unlikely for our system any curved relationship such as that found by Klopman under other experimental conditions.[12] The acetonitrile data for the three halobenzene series gave essentially the same picture, although with a fewer number of experimental points.

Our two-electrode cell, designed to avoid the large *iR* corrections encountered with more conventional cells,[13] employed a Ag|AgBr anode. Although capable of short-term reproducibility of 0.01 V, this electrode has been found to lack suitable long-term stability for use as a reference electrode in precise work[5b] and half-wave potentials referred to it may be in error by several centivolts.[14] This uncertainty may slightly affect the fitting of straight lines to the experimental points but does not alter the conclusions drawn from the data.

Discussion

The positive slopes for the half-wave potential *vs.* σ plots of our data and the similar results obtained by others[5b,8,11,12,15] indicate clearly that the carbon of the carbon–halogen bond is becoming negative as the system moves into the transition state of the potential-determining step. This definitely rules out the SN1 or carbonium ion mechanism I, as well as any blend of the ionic mechanism[10] in which SN1 character predominates over carbanion (or SN2) character, *i.e.*, electrons are removed by the departing halide ion more rapidly than they are replaced by the cathode. On the other hand, the experimental findings are compatible with the carbanion mechanism II or the much more likely form of the ionic mechanism in which carbanion character predominates over SN1 character. The results are also consistent with the formation of a negatively charged radical anion IV or with the direct formation of a free radical without the intervention of radical anion III, provided that the carbon acquires a partial negative charge during the displacement of the halide ion by an electron.

The unexpectedly easy reduction of 9-bromotriptycene (half-wave potential of −1.42 V compared to −1.97 V for 1-bromobicyclo[2.2.2]octane)[5a] is further evidence for a negatively charged transition state. The three benzene rings are oriented so that there cannot be appreciable conjugation with the carbon–bromine system during reduction, but the data can be explained readily in terms of the stabilizing effect of the electronegative benzene rings[16] on the negatively charged carbon atom. The increasing ease of reduction as more halogens are added to an individual carbon atom[17] can also be cited in support of the buildup of negative charge during reduction.

It could not have been predicted that σ^- values would give more linear plots against half-wave potentials than the conventional σ values. Nevertheless, the result is not surprising, since the cross-conjugative effects between *para* substituents with unshared electrons and the carbonyl group of benzoic acid are included in σ values but are not present in this system. At the other end of the σ scale, the σ values apparently seriously underestimate the interaction between the electron-rich transition state and such strong electron-attracting groups as —COR, —C≡N, and $—NR_3^+$. It is also pertinent to note that the *p*-SMe point which fell far from the line in Streitwieser and Perrin's plot for benzyl chlorides[8] will be moved almost halfway toward the line if a σ^- value of 0.16 based on the ionization of substituted phenols[18] is used instead of the conventional σ value of 0.00.

Experimental Section

A Sargent Model XXI polarograph was used as the voltage source. Polarograms were recorded on a Moseley Model 135 X-Y

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(13) F. L. Lambert and K. Kobayashi, *J. Am. Chem. Soc.*, **82**, 5324 (1960).

(14) Referee's comment.

(15) After the original draft of this paper had been submitted, Hussey and Diefenderfer published half-wave potentials and $\rho\sigma$ plots for the reduction of a considerable number of *ortho-*, *meta-*, and *para-*substituted iodo- and bromobenzenes in aqueous solution (W. W. Hussey and A. J. Diefenderfer, *J. Am. Chem. Soc.*, **89**, 5359 (1967)). Their data are consistent with ours and further support the idea of a negatively charged transition state.

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(17) M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949).

(18) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **74**, 1058 (1952).

recorder, the voltage applied across the cell being measured on the X axis and the resulting current being determined by observing the voltage drop across a standard resistor connected between the Y input terminals of the recorder.

The capillary constant for the dropping mercury electrode ($m^{2/3}t^{1/6}$) was 1.41 mg$^{2/3}$ sec$^{-1/2}$ at -0.5 V *vs.* Ag|AgBr in dimethylformamide containing 2×10^{-2} *M* tetraethylammonium bromide. The anode was a 10-cm length of 1-mm diameter silver wire, coiled in a spiral about the lower end of the dropping mercury capillary. All polarograms were determined at 25.0 ± 0.2° with thoroughly deaerated solutions which were between 4×10^{-4} and 5×10^{-4} *M* in substrate and 2×10^{-2} *M* in tetraethylammonium bromide. Cell resistance, measured with a Serfass Model RC M15 conductivity bridge and a tiny platinized platinum electrode sealed through the end of a glass tube which replaced the dropping mercury capillary, was approximately 1300 ohms for the dimethylformamide system and 800 ohms for the acetonitrile system.

3-Iodobiphenyl was synthesized from 3-aminobiphenyl[19] and *p*-iododimethylaniline from dimethylaniline.[20] The *p*-iodo, *p*-bromo, and *m*-chloro derivatives of trimethylanilinium bromide were prepared by methylation of the corresponding dimethylaniline derivative.[20] A sample of *p*-iodobenzophenone was furnished by Professor Albert J. Fry. All other halogen compounds were obtained from Eastman Organic Chemicals or K & K Laboratories, Inc.

Fisher reagent grade dimethylformamide was purified by refluxing over calcium hydride (5 g/1.5 l.) for 1 hr at a pressure of approximately 1 mm, and then distilling under vacuum through a 24-in. column packed with glass helices. The first 10% of the distillate was discarded as well as any other 10% fraction which showed appreciable decomposition before a cathode potential of -2.3 V *vs.* Ag|AgBr was reached. Acetonitrile (Matheson Coleman and Bell), refluxed for 10 min over sodium hydride (1 g/l.) and distilled rapidly,[21] was found to contain considerable reducible impurity. Satisfactorily pure solvent could be obtained, however, by repeating the reflux with a fresh portion of sodium hydride and then distilling at atmospheric pressure through a 24-in., helix-packed column; the resulting solvent was usable to about -2.3 V *vs.* Ag|AgBr.

Eastman reagent grade tetraethylammonium bromide was recrystallized by adding 27 ml of anhydrous ether to a solution of 3 g of tetraethylammonium bromide in 9 ml of 95% ethanol. The precipitate was dried *in vacuo* for 36–48 hr before use and stored in a vacuum desiccator over silica gel for a maximum of 2 weeks.

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(19) E. Campaigne and W. B. Reid, Jr., *J. Am. Chem. Soc.*, **68**, 1663 (1946).

(20) T. H. Reade, *J. Chem. Soc.*, **125**, 148 (1924).

(21) G. A. Forcier and J. W. Olver, *Anal. Chem.*, **37**, 1447 (1965).

Electrophilic Substitution at Saturated Carbon. XXXVIII. Survey of Substituent Effects on Stereochemical Fate of Fluorenyl Carbanions[1]

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Contribution No. 2147 from the Department of Chemistry, University of California at Los Angeles, Los Angeles, California 90024. Received November 1, 1967

Abstract: A survey has been made of the values of k_e/k_α (one-point rate constant for base-catalyzed isotopic exchange over that for racemization) for five deuterated, optically active, 9-methylfluorenyl systems substituted with amido, nitro, and cyano groups. The syntheses of optically active 9-deuterio-9-methylfluorenyl systems with the following substituents are described: 2-cyano (II), 2-nitro (III), 3-N,N-dimethylcarboxamido (IV), and 2-N,N-dimethylcarboxamido-7-nitro (V). The k_e/k_α values of these compounds and those of 2-(N,N-dimethylcarboxamido)-9-methylfluorene (I) were found to vary markedly with changes in substituent character, substituent position, media, and pK_a relationship between carbon acid and the conjugate acid of the base employed. In tetrahydrofuran-*t*-butyl alcohol with tri-*n*-propylamine as base, the 2-amido system I undergoes isotopic exchange with retention of configuration under conditions that the other four systems (II–V) give isoracemization (intramolecular racemization). The 2-amido system I gives high retention with *n*-propylamine in tetrahydrofuran, whereas the 3-amide IV and 2-amido-7-nitro system V give low retention and total racemization, respectively, under the same conditions. The 2- and 3-amides in methanol–potassium methoxide gave predominantly racemization with exchange, and reaction rates separated only by a factor of 2. With nitro amide V, substitution of *p*-methylaniline in tetrahydrofuran for *n*-propylamine in tetrahydrofuran changed the stereochemical result from total racemization with exchange to high net retention. A rough comparison of the kinetic acidities of the hydrocarbons is made. These facts are interpreted in terms of the behavior of ammonium carbanide ion pairs, whose stereochemical fates depend on the relative rates of up to four fast processes: ion-pair dissociation, alkylammonium ion rotation, carbanion rotation, and proton capture. Particularly striking is the importance of charge distribution in the anion in making carbanion rotation competitive with the other processes.

A prior paper reported the preparation of and results of a survey of the stereochemical course of the base-catalyzed hydrogen isotopic exchange of carbon acid I with medium.[2] Values of k_e/k_α (rate constant for isotopic exchange over that for racemization) determined from single kinetic points were used as a qualitative probe. Thus, when $k_e/k_\alpha > 1$, isotopic exchange occurs with retention of configuration. When $k_e/k_\alpha = 1$, exchange goes with racemization. With $k_e/k_\alpha = 0.5$, exchange occurs with net inversion, and with $k_e/k_\alpha < 0.5$, racemization without exchange or *isoracemization* is observed. In this survey, values of k_e/k_α as high as >56 and as low as 0.69 were observed. Later detailed

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(1) This research was sponsored by the U. S. Army Research Office, Durham, N. C. The authors extend their thanks.

(2) D. J. Cram and L. Gosser, *J. Am. Chem. Soc.*, **86**, 5445 (1964).