

rectly bound to the catalytic center, which cause the preferential absorption of one antipode at the transition metal.

Further work is in progress to establish the possible influence of different metal alkyls and transition metals on the stereoelectivity of the process and to obtain more information on the structure of the optically active polymers we have synthesized.

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### Stereochemical Consequences of Ion-Pair Formation Involving Carbanions

Sir:

Earlier work<sup>1</sup> demonstrated that base-catalyzed hydrogen isotope exchange between hydroxylic solvent and the benzyl position of 2-phenylbutane (I) could be made to occur with high retention, total racemization, or net inversion, depending on the solvent used. The

With ammonia as base,  $k_e$  and  $k_\alpha$  increased by an estimated  $10^5$  to  $10^7$  in passing from *tert*-butyl alcohol to tetrahydrofuran to methanol to dimethyl sulfoxide (runs 3, 1, 10, and 9). This fact points to formation of a highly charged transition state from noncharged starting materials. With propylamine as base in tetrahydrofuran, addition of either lithium bromide or propylammonium acetate (0.5 *N*) increased the rates by  $10^2$  to  $10^3$  (runs 2, 5, and 7). A similar salt effect has been observed in carbonium ion formation from uncharged starting materials in nonpolar solvents.<sup>3</sup> These striking medium effects point to carbanion formation in the isotopic exchange reactions.

The values of  $k_e/k_\alpha$  varied from about 148 (exchange with high retention) to 1 (complete racemization) to 0.69 (high inversion), depending on the base-solvent system. In tetrahydrofuran with ammonia as base,  $k_e/k_\alpha \sim 148$  (run 1). The formulas provide an interpretation of this result.<sup>1b</sup>

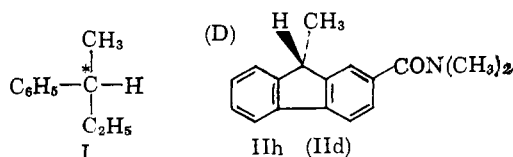
These data provide strong evidence for formation of an ammonium carbanide ion pair, which dissociates in tetrahydrofuran much slower than the ammonium ion rotates and collapses ( $k_{-1}$  and  $k_3 \gg k_2$ ). Isotope effect evidence for  $k_{-1} > k_2$  was obtained in other

TABLE I  
STEREOCHEMICAL COURSE OF BASE-CATALYZED HYDROGEN-DEUTERIUM EXCHANGE AT THE 9-POSITION OF 2-[N,N-DIMETHYL-CARBOXAMIDO]-9-METHYLFLUORENE (IIh) OR 9-DEUTERATED MATERIAL (IId)<sup>a</sup>

Run no.	Start. matl. Type	Concn., <i>M</i>	Base Type	Concn., <i>M</i>	Solvent	Temp., C°	Time, hr.	% <sup>c</sup> Rac.	% <sup>c</sup> Exch.	$k_e/k_\alpha^d$	Steric course
1	II d	0.020	NH <sub>3</sub>	0.2	THF <sup>e</sup>	145	5	2	95	148	High ret.
2	II d	0.022	PrNH <sub>2</sub>	0.5	THF <sup>e</sup>	145	1	7	100	>56	High ret.
3	II d	0.028	NH <sub>3</sub>	0.8	<i>t</i> -BuOH	200	3	8	100	>50	High ret.
4	II d	0.020	C <sub>6</sub> H <sub>5</sub> OK	<0.1	C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>5</sub> OH <sup>f</sup>	75	<2	1.2	20	18	High ret.
5	II d	0.022	PrNH <sub>2</sub>	0.5	THF-LiBr <sup>g</sup>	75	1	40	94	5.6	Ret.
6	II d	0.023	Pr <sub>3</sub> N	1	C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>5</sub> OH <sup>f</sup>	145	4.3	6	25	5	Ret.
7	II d	0.042	PrNH <sub>2</sub>	0.5	THF-PrNH <sub>3</sub> OAc <sup>g</sup>	75	2	60	93	3	Ret.
8	II h	0.06	KHCO <sub>3</sub>	0.06	DOCH <sub>2</sub> CH <sub>2</sub> OD <sup>h</sup>	50	4.7	46	48	1	Rac.
9	II d	0.017	NH <sub>3</sub>	0.2	(CH <sub>3</sub> ) <sub>2</sub> SO	25	1.5	9	8	1	Rac.
10	II d	0.032	NH <sub>3</sub>	0.8	CH <sub>3</sub> OH	75	4	31	31	1	Rac.
11	II h	0.16	C <sub>6</sub> H <sub>5</sub> OK <sup>i</sup>	0.024	(CH <sub>3</sub> ) <sub>3</sub> COD <sup>j</sup>	25	7	54	50	0.9	Rac.
12	II d	0.12	Pr <sub>3</sub> N	0.7	CH <sub>3</sub> OH	75	13	59	46	0.69	High inv.
13	II d	0.14	Et <sub>3</sub> N	0.5	THF-LiBr <sup>g</sup>	145	42	72	25	0.23	...

<sup>a</sup> 0.97-0.99 atom of deuterium per molecule. <sup>b</sup>  $\alpha_{\text{obs}} > 0.6^\circ$ . <sup>c</sup> Deuterium analyses performed through infrared measurements at 1150 cm.<sup>-1</sup> using standards of known isotopic composition. <sup>d</sup> Calculated assuming  $k_\alpha^H/k_\alpha^D = 1$ . <sup>e</sup> THF = tetrahydrofuran. <sup>f</sup> 10% phenol by weight. <sup>g</sup> 0.5 *M* in salt. <sup>h</sup> 1.98 atoms of deuterium per molecule. <sup>i</sup> Solution was 0.024 *M* in phenol. <sup>j</sup> 0.96 atom of deuterium per molecule.

relatively low acidity of 2-phenylbutane coupled with steric constraints to planarity of the derived carbanion placed both experimental and theoretical limitations on the system.

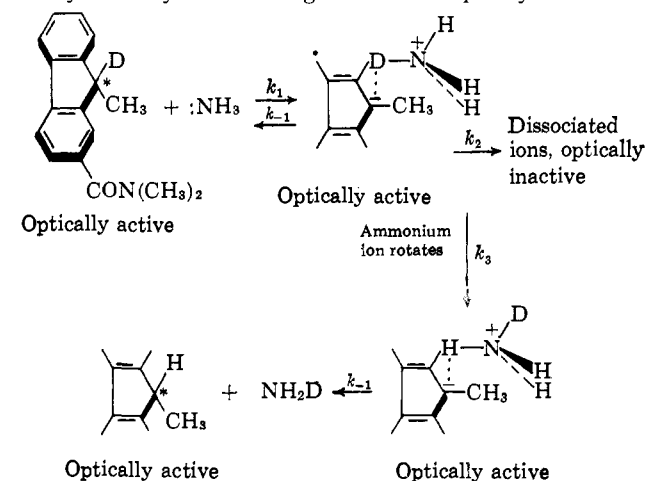


System II, with an estimated  $pK_a$  of 23 (I is probably around 50), gives an anion which tends to be planar, since it is isoelectronic with and has the shape of anthracene. Optically pure II, deuterated and nondeuterated in the 9-position, was prepared by conventional means.<sup>2</sup> The relative rates (one point) of racemization ( $k_\alpha$ ) and isotopic exchange ( $k_e$ ) have been roughly determined in a variety of solvent-base systems. The experimental conditions and results are tabulated in Table I.

(1) (a) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961); (b) D. J. Cram, *Chem. Eng. News*, **41**, No. 33, 92 (1963).

(2) All new compounds gave carbon-hydrogen analyses within 0.3% of theory.

systems.<sup>4</sup> The intramolecular character of the base-catalyzed allylic rearrangement of 3-phenyl-1-butene



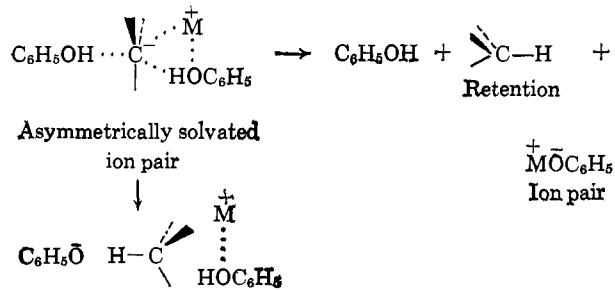
(3) S. Winstein, S. Smith, and D. Darwish, *J. Am. Chem. Soc.*, **81**, 5511 (1959).

(4) D. J. Cram, D. A. Scott, and W. D. Nielsen, *ibid.*, **83**, 3696 (1961).

to *cis*-2-phenyl-2-butene in deuterated hydroxylic solvents also supports the concept that hydrogen-bonded carbanion collapse to hydrocarbon occurs at rates comparable to the rates of solvent molecule interchange at the carbanionic site.<sup>5</sup>

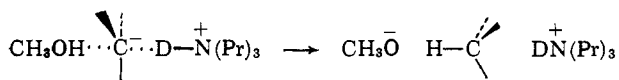
Exchange occurred with high retention with either ammonia or propylamine in tetrahydrofuran (runs 1 and 2), or ammonia in *tert*-butyl alcohol (run 3), but gave racemization with ammonia in either methanol or dimethyl sulfoxide (runs 9 and 10). In these latter solvents, ion-pair dissociation is apparently faster than other processes ( $k_2 > k_3$  and possibly  $k_{-1}$ ). Thus in nondissociating solvents, asymmetric solvation of a planar or near-planar carbanion accounts for the results, whereas in dissociating solvents, a symmetrically solvated carbanion is formed.

Exchange went with high retention in benzene-phenol with either potassium phenoxide or tripropylamine as base (runs 4 and 6), but gave racemization in *tert*-butyl alcohol (run 11) with potassium phenoxide. Stereospecificity is undoubtedly dependent on very rapid proton transfers, which are in turn dependent on large  $pK_a$  differences between the solvent (or proton donor) and substrate. With phenol (or ammonium ions), the difference is about 13  $pK_a$  units, whereas with *tert*-butyl alcohol, it is only about 4  $pK_a$  units. Retention in runs 4 and 6 is probably dependent on the fact that greater charge separation would result from capture of the carbanion from the rear than from the side of the leaving group.<sup>6</sup> The low dielectric constant of the medium would suppress such a process. The potassium ion also probably plays a solvent-orienting role at the front side.



Ion separated by inverted product

With tripropylamine as base in methanol, high inversion was observed (run 12). In this dissociating solvent, charge separation by back-side proton capture is not serious. The tripropylammonium ion shields the front side, thus promoting back-side proton capture.



Run 13 was conducted in tetrahydrofuran with triethylamine as base, and lithium bromide was added so a reasonable temperature could be employed. Although attempts were made to exclude moisture, some undoubtedly was present, since  $k_e/k_a = 0.23$ . In the complete absence of moisture,  $k_e/k_a$  should become exceedingly low valued, since tetrahydrofuran or tripropylamine should be very poor proton sources.<sup>7</sup>

(5) D. J. Cram and R. T. Uyeda, *J. Am. Chem. Soc.*, **84**, 4358 (1962).

(6) The author is indebted to Dr. A. Streitwieser for first pointing out this relationship (private communication).

(7) This research was sponsored by the U. S. Army Research Office, Durham, N. C.

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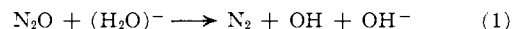
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## Reactivities of the Primary Reducing Species Formed in the Radiolysis of Aqueous Solutions

Sir:

It is currently recognized that two primary reducing species are produced by the action of ionizing radiations on aqueous systems, *viz.* the electron (or negative polaron<sup>1</sup>), represented here by  $(H_2O)^-$ , and a dehydrogenating species,<sup>2,3</sup> presumed to be a hydrogen atom, which is designated in the following by  $H^\alpha$ . Considerable interest has recently centered around the use of pulse radiolysis techniques to determine the absolute rates of reaction of  $(H_2O)^-$  with different solutes.<sup>4</sup> In this communication we give some *relative* rates of reaction of the two primary species toward different solutes. All of these experiments have been carried out with  $Co^{60}$   $\gamma$ -rays in the absence of oxygen.

1. **Reactivity of  $(H_2O)^-$ .**—It has been shown<sup>5</sup> that  $N_2O$  has a relatively high reactivity toward  $(H_2O)^-$ , leading to the formation of nitrogen according to

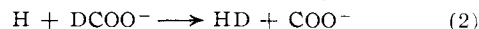


Substances which compete efficiently with  $N_2O$  for  $(H_2O)^-$  lower the nitrogen yield, and the relative rates can thus be obtained. Solutions of  $N_2O$  ( $1.6 \times 10^{-2} M$ ) at neutral pH have been used for these experiments, the yields of nitrogen being determined mass spectrometrically. Table I, column a, shows some of the results obtained, taking  $k[(H_2O)^- + N_2O] = 1.00$ .

Comparison with relative rate constants calculated from the data of Gordon, *et al.*<sup>4</sup> (Table I, column c), shows good agreement for several of the solutes investigated.

Table I shows that nitrate ions also have a high reactivity toward the radiation-produced electrons. The reduction of nitrate to nitrite has been studied in sodium nitrate solutions containing 2-propanol ( $10^{-1} M$ ), nitrite being determined by the method of Endres and Kaufman.<sup>6</sup> The observed yields of nitrite were  $G(NO_2^-) = 2.52$  and  $G(NO_2^-) = 2.86$  at sodium nitrate concentrations of  $10^{-3}$  and  $10^{-2} M$ , respectively. Addition of other electron acceptors to the nitrate-2-propanol solutions led to a reduction in the radiolytic yield of nitrite. Relative rates compared to nitrate were then calculated assuming simple competition, in which nitrite is formed only as a consequence of reaction of  $(H_2O)^-$  with nitrate. Some results normalized to  $k[(H_2O)^- + N_2O] = 1.00$  are given in Table I, column b. It can be seen that there is a good measure of agreement with the corresponding relative rates obtained by the  $N_2O$  system.

2. **Reactivity of Hydrogen Atoms ( $H^\alpha$ ).**—In the radiolysis of deaerated aqueous solutions of sodium deuterioformate containing another organic solute (RH) which can be dehydrogenated, the ratio  $G(HD)/G(H_2)$  will be governed by the competing reactions



If the experimental conditions are such that  $H^\alpha$  is the only dehydrogenating species entering the above competition, measurement of the yields of HD and of  $H_2$  should lead directly to the rate ratio  $k_{(H^\alpha + DCOO^-)}/k_{(H^\alpha + RH)}$ . These conditions are attained if  $N_2O$  is

(1) J. Weiss, *Nature*, **186**, 75 (1960).

(2) J. T. Allan and G. Scholes, *ibid.*, **197**, 218 (1960).

(3) J. Rabani, *J. Am. Chem. Soc.*, **84**, 868 (1962); J. Rabani and G. Stein, *J. Chem. Phys.*, **37**, 1867 (1962).

(4) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *J. Am. Chem. Soc.*, **85**, 1375 (1963); *Discussions Faraday Soc.*, Notre Dame, Paper No. 14, (1963).

(5) F. S. Dainton and D. B. Peterson, *Nature*, **186**, 878 (1960); *Proc. Roy. Soc. (London)*, **A267**, 443 (1962).

(6) G. Endres and L. Kaufman, *Ann.*, **172**, 530 (1940).