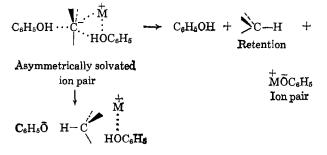
to *cis*-2-phenyl-2-butene in deuterated hydroxylic solvents also supports the concept that hydrogen-bonded carbanion collapse to hydrocarbon occurs at rates comparable to the rates of solvent molecule interchange at the carbanionic site.⁵

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 tertbutyl 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 p K_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.⁶ 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.

$$CH_{3}OH \cdots C \overline{C} \cdots D - N(Pr)_{3} \longrightarrow CH_{3}\overline{O} H - C DN(Pr)_{3}$$

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 $k_e/k_{\alpha} = 0.23$. In the complete absence of moisture, k_e/k_{α} should become exceedingly low valued, since tetrahydrofuran or tripropylamine should be very poor proton sources.⁷

(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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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 polaron¹), represented here by $(H_2O)^-$, and a dehydrogenating species,^{2,3} presumed to be a hydrogen atom, which is designated in the following by H^{α}. 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.⁴ 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 Co⁶⁰ γ -rays in the absence of oxygen.

1. Reactivity of $(H_2O)^-$.—It has been shown⁶ that N₂O has a relatively high reactivity toward $(H_2O)^-$, leading to the formation of nitrogen according to

$$O + (H_2O)^- \longrightarrow N_2 + OH + OH^-$$
(1)

Substances which compete efficiently with N₂O for $(H_2O)^-$ lower the nitrogen yield, and the relative rates can thus be obtained. Solutions of N₂O (1.6 × 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.*⁴ (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.⁶ The observed yields of nitrite were $G(NO_2^{-}) = 2.52$ and $G(NO_2^{-}) = 2.86$ at sodium nitrate concentrations of 10^{-8} 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 (H₂O)⁻ 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 N₂O system.

2. Reactivity of Hydrogen Atoms (H^{α}) .—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

$$H + DCOO^{-} \longrightarrow HD + COO^{-}$$
(2)

$$H + RH \longrightarrow H_2 + R.$$
(3)

If the experimental conditions are such that H^{α} is the only dehydrogenating species entering the above competition, measurement of the yields of HD and of H₂ should lead directly to the rate ratio $k_{(H^{\alpha} + DCOO^{-})}/k_{(H + RH)}$. These conditions are attained if N₂O 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).
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- (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).

TABLE I

Reactivities of Different Solutes toward (H_2O) -, Normalized Relative to the Reaction with N₂O

	Relative reactivity, R					
	a $\ln \text{ the } N_2 O \text{ systems}$ $[N_2 O] = 16 \text{ m}M$		b 1n the NO3 ⁻ systems {NO3 ⁻] = 1 mM		c From absolute rate measurements ^e	
Solute,						
S	$\{S\}, mM$	R	[S], mM	R	R^{a}	
$Cu^{2+}(CuSO_4)$	0.28 - 4.75	3.85 ± 0.30			3.81 ± 0.6	
H +	1-63	1.70 ± 0.15			2.72 ± 0.5	
Thymine	23	1.67 ± 0.15	0.44	2.08 ± 0.30		
NO_3^-	10	1.17 ± 0.15	10^{b}	1.19 ± 0.15	1.27 ± 0.2	
N_2O		1.00		1.00	1.00	
Fe(CN) ₆ ³⁻	10	0.89 ± 0.07	1	0.88 ± 0.08	$0.92 \pm 0.15^{\circ}$	
Acetone	10-100	0.67 ± 0.05	2	1.01 ± 0.10	0.68 ± 0.07	
NO_2^-	100	0.49 ± 0.05				
$\rm CO_2$	20^{d}	0.46 ± 0.04		• • •	0.88 ± 0.2	
Chloroacetate	5 - 200	0.19 ± 0.01	5	0.14 ± 0.02		
$H_2PO_4^-$			300	$2.22 \pm 0.3 \times 10^{-3}$		

^a Maximum solute concentrations in the range 0.1-0.3 mM. ^b Solution contained $16 \text{ m}M \text{ N}_2\text{O}$. ^c At the corresponding ionic strength.

^d Solution contained 8 mM N₂O; pH 3.5-4.0. ^e See ref. 4.

also present, since possible complications arising from reactions of $(H_2O)^-$ with the organic solutes, and with water to give hydrogen atoms, will be suppressed owing to the occurrence of reaction 1. Table II includes some relative rates obtained using this technique, $k_{(H\alpha + DCOO^-)}$ being taken as 1.0.

In those instances where the solutes do not yield hydrogen on reaction with H^{α} (e.g., allyl alcohol, $Fe(CN)_{6}^{3-}$) the system {N₂O (1.6 × 10⁻² M) + 2propanol (10⁻¹ M)} has been used. Here, hydrogen arises from the molecular process and from the reaction

 $(CH_3)_2CHOH + H \longrightarrow (CH_3)COH + H_2$ (4)

which is in competition with hydrogen atoms reacting with a solute (\mathbf{X}) .

 $H + X \longrightarrow XH$ (5)

From the measured hydrogen yields, the rates of reaction of the solutes relative to 2-propanol (k_4/k_5) have been obtained and these then normalized to $k_{(H^{\alpha} + DCOO^{-})} = 1.0$ (Table II). It is not always necessary to have N₂O present in these experiments, since the solute itself may scavenge the $(H_2O)^{-}$. This latter method is, in fact, somewhat similar to that used by Rabani and Stein⁸ using either ferricyanide or nitrite and several organic solutes which can be dehydrogenated.

TABLE II

Reactivity of Different Solutes toward Hydrogen Atoms (Ha) Normalized Relative to the Reaction with $DCOO^-$

Solute ^a	{Solute], mM	{DCOO ⁻], m <i>M</i>	{Isopropyl], mM	Relative reactivity
Fe(CN)63 -	1		100	180 ± 40
Allyl alcohol	3		100	104 ± 23
Benzyl alcohol	4		100	29 ± 6
Cu ² -(CuSO ₄)	0.28-4.75		100	$28~\pm~7$
HC00-	10	10		6.6 ± 0.7
NO2 -	100		100	6.1 ± 1.0
2-Propanol	10	10		2.25 ± 0.2
Glyoxalate	10	5		1.6 ± 0.1
NO3 -	100		100	1.1 ± 0.4
DC00-				1.0
Ethanol	10	3		0.7 ± 0.1
Ethylene glycol	10	20		$4.3 \pm 0.5 \times 10^{-1}$
Chloroacetate	10	2		$8.4 \pm 1.2 \times 10^{-2}$
Methanol	100	10		$7.4 \pm 0.8 \times 10^{-2}$
Acetone	100	2		$2.8 \pm 0.3 \times 10^{-2}$
Acetate	100	2		$1.2 \pm 0.1 \times 10^{-2}$
t-Butyl alcohol	100	1		$4.4 \pm 0.7 \times 10^{-3}$

^{*a*} All solutions contained N_2O (16 mM).

These authors have reported that the relative reactivities of ferricyanide, nitrite, formate (HCOO⁻), and 2-propanol toward H^{α} are in the ratio 1:0.22:0.055: 0.013. The present work gives the corresponding ratio as 1:0.034:0.037:0.012 which, apart from the case of nitrite, is in quite good agreement.

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A Neutron Diffraction Study of α -Lead Azide Sir:

Earlier studies of lead azide were made by Miles,¹ Hughes,² Pfefferkorn,³ Azaroff,⁴ and Saha.⁵ The orthorhombic unit cell has dimensions a = 6.63, b =11.31, and c = 16.25 Å. With 12 molecules per unit cell, the density is 4.71 g./ml. On the basis of the diffraction effects, the space group can be either Pnam or Pna2₁. The latter was chosen because a threedimensional refinement⁵ of the lead parameters showed that the *R*-factor comes down considerably if the noncentrosymmetric space group is assumed.

Azaroff⁴ determined the lead positions from a two dimensional X-ray analysis, but failed to locate the nitrogen atoms because the lead atoms dominate the intensities of the X-ray data. Neutron data for the 0kl reflections were collected by Danner and Kay at the Brookhaven National Laboratory. Although the neutron scattering lengths for lead and nitrogen are approximately equal, an attempt to obtain a trial structure from a Patterson synthesis of this data failed, due to a considerable overlap of vector peaks. However, a three-dimensional X-ray analysis at Pennsylvania State University by Saha⁵ resulted in a trial structure despite the fact that many difficulties were encountered both in collecting and analyzing the data.

Using the neutron data, a two-dimensional refinement of these parameters was begun. Initially, a Fourier difference synthesis was used. However, after a few cycles it became apparent that further refinement using Fourier projections would be difficult because of the considerable overlap of lead and nitrogen peaks. Least-squares refinement was not satisfactory

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