

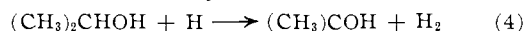
TABLE I
REACTIVITIES OF DIFFERENT SOLUTES TOWARD $(\text{H}_2\text{O})^-$, NORMALIZED RELATIVE TO THE REACTION WITH N_2O

Solute, S	Relative reactivity, R					
	a In the N_2O systems [N_2O] = 16 mM		b In the NO_2^- systems [NO_2^-] = 1 mM		c From absolute rate measurements ^e	
	[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
$\text{Fe}(\text{CN})_6^{3-}$	10	0.89 ± 0.07	1	0.88 ± 0.08	...	0.92 ± 0.15^c
Acetone	10-100	0.67 ± 0.05	2	1.01 ± 0.10	...	0.68 ± 0.07
NO_2^-	100	0.49 ± 0.05
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 M. ^b Solution contained 16 mM N_2O . ^c At the corresponding ionic strength. ^d Solution contained 8 mM N_2O ; pH 3.5-4.0. ^e See ref. 4.

also present, since possible complications arising from reactions of $(\text{H}_2\text{O})^-$ 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, $k_{(\text{H}^\alpha + \text{DCOO}^-)}$ being taken as 1.0.

In those instances where the solutes do not yield hydrogen on reaction with H^α (e.g., allyl alcohol, $\text{Fe}(\text{CN})_6^{3-}$) the system $\{\text{N}_2\text{O} (1.6 \times 10^{-2} \text{ M}) + 2\text{-propanol} (10^{-1} \text{ M})\}$ has been used. Here, hydrogen arises from the molecular process and from the reaction



which is in competition with hydrogen atoms reacting with a solute (X).



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 $k_{(\text{H}^\alpha + \text{DCOO}^-)} = 1.0$ (Table II). It is not always necessary to have N_2O present in these experiments, since the solute itself may scavenge the $(\text{H}_2\text{O})^-$. 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 (H^α) NORMALIZED RELATIVE TO THE REACTION WITH DCOO^-

Solute ^a	[Solute], mM	[DCOO^-], mM	[Isopropyl], mM	Relative reactivity
$\text{Fe}(\text{CN})_6^{3-}$	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 ± 7
HCOO^-	10	10	...	6.6 ± 0.7
NO_2^-	100	...	100	6.1 ± 1.0
2-Propanol	10	10	...	2.25 ± 0.2
Glyoxalate	10	5	...	1.6 ± 0.1
NO_3^-	100	...	100	1.1 ± 0.4
DCOO^-	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	...	$1.2 \pm 0.1 \times 10^{-2}$
<i>t</i> -Butyl alcohol	100	1	...	$4.4 \pm 0.7 \times 10^{-2}$

^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.

Acknowledgment.—We thank Professor J. J. Weiss for his encouragement of this work and Mr. P. Kelly for mass spectrometry. We are indebted to the U. S. Army for financial support, through Contract No. DA-91-591-EUC-2750.

LABORATORY OF RADIATION CHEMISTRY
SCHOOL OF CHEMISTRY
THE UNIVERSITY
NEWCASTLE UPON TYNE, 1
ENGLAND

A. APPLBY
G. SCHOLES
M. SIMIC

RECEIVED AUGUST 19, 1963

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 three-dimensional refinement⁵ of the lead parameters showed that the R -factor comes down considerably if the non-centrosymmetric 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

- (1) F. D. Miles, *J. Chem. Soc.*, 2532 (1931).
- (2) E. W. Hughes, Ph.D. Thesis, Cornell University, 1935.
- (3) G. Pfefferkorn, *Z. Naturforsch.*, **3**, 364 (1948).
- (4) L. V. Azaroff, *Z. Krist.*, **107**, 362 (1956).
- (5) P. Saha, private communication.