

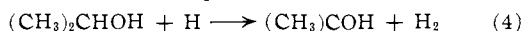
TABLE I
REACTIVITIES OF DIFFERENT SOLUTES TOWARD $(\text{H}_2\text{O})^-$, NORMALIZED RELATIVE TO THE REACTION WITH N_2O

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	$2.22 \pm 0.3 \times 10^{-3}$...	

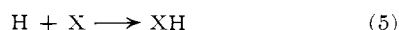
^a Maximum solute concentrations in the range 0.1-0.3 M. ^b Solution contained 16 mM N_2O . ^c At the corresponding ionic strength. ^d Solution contained 8 mM N_2O ; pH 3.5-4.0. ^e See ref. 4.

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	...	$1.2 \pm 0.1 \times 10^{-2}$
t-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.

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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.

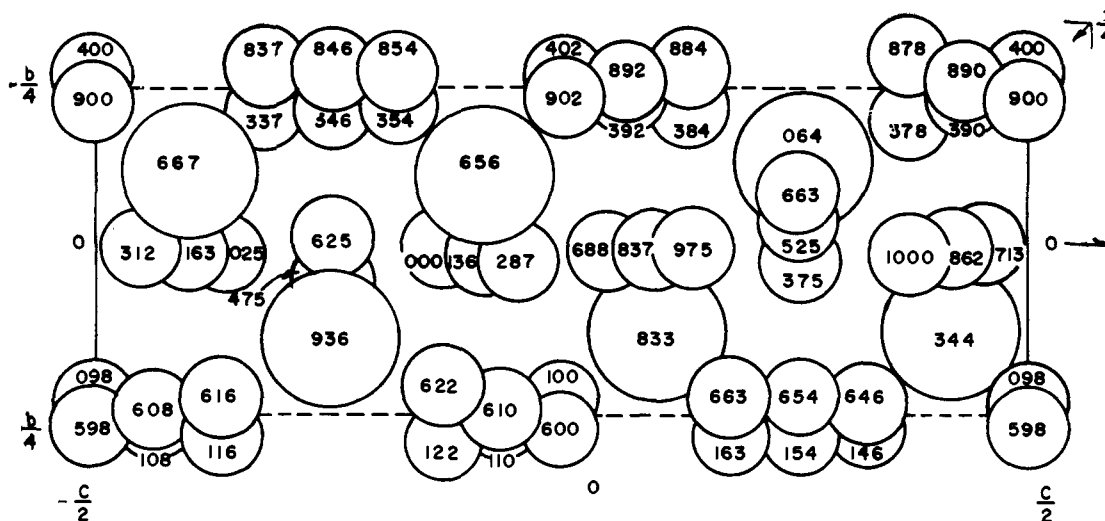


Fig. 1.—Diagram to illustrate the packing arrangement within the crystal. The lead atoms are represented by the large circles and the nitrogen by the small circles.

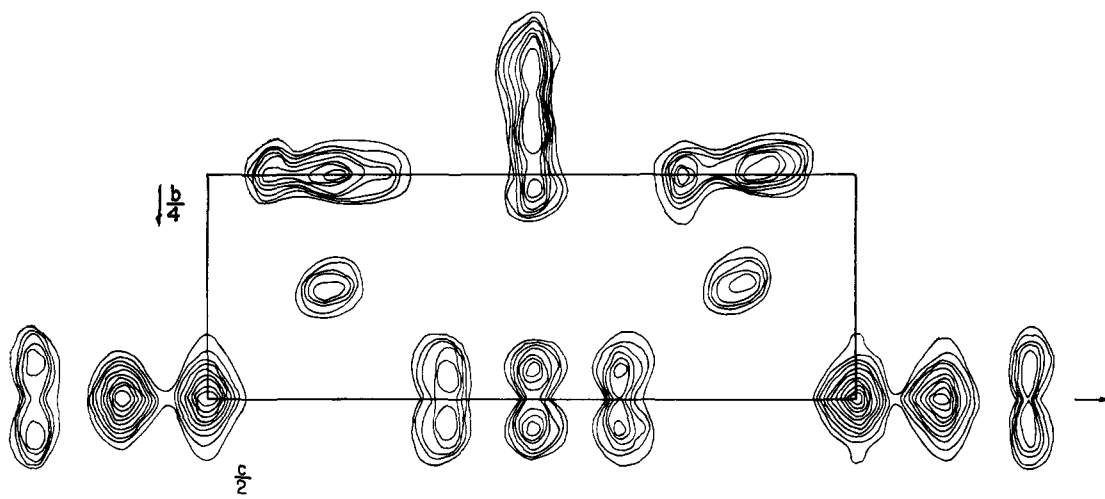


Fig. 2.— $0kl$ neutron scattering density map for one asymmetric unit. Contours are at arbitrary intervals.

either, since there was also the possibility that the data contained systematic errors. Finally it was decided to use a combination of these two analyses. The y - and z -coordinates for each cycle were determined by averaging the values obtained from each type of analysis. In addition, the nitrogen coordinates (including the x parameters) were adjusted further, assuming that all azide groups were linear. The thermal parameters were determined by the least-squares refinement. The conventional $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was reduced from an initial value of 0.340 to 0.070. The parameters are listed in Table I.

The average standard deviation of the y - and z -coordinates is 0.06 Å. There are three reasons⁶ for this high value: (1) the central curvatures of the atoms are rather small; (2) the structure does not have a center of symmetry and all atoms are in general positions; and (3) the number of refined parameters (63) is not much less than the number of independent reflections (102).

The lead atoms (designated 2 and 3 in Table I) have seven nearest nitrogen neighbors and the remaining lead atom has eight. The Pb-N distance ranges from 2.48 to 2.92 Å. The packing is illustrated in Fig. 1.

From bond energy considerations, Pauling and Brockway⁷ have shown that the linear azide groups will

(6) Cf. H. Lipson and W. Cochran, "The Determination of Crystal Structures. The Crystalline State," Vol. III, G. Bell and Sons, London, 1953, pp. 308-309.

be asymmetric if the bonding is homopolar. Evidence for this appears in the $0kl$ neutron scattering density map which is shown in Fig. 2 and also in the calculated

TABLE I

	x	y	z	$B, \text{Å}^2$
Pb(1)	0.064	-0.140	0.247	2.08
Pb(2)	.344	.121	.415	2.23
Pb(3)	.333	.122	.092	0.68
N	.665	.214	.178	1.30
N	.654	.214	.250	1.35
N	.646	.214	.321	1.69
N	.596	.266	.498	1.24
N	.607	.235	.567	1.51
N	.616	.205	.632	3.07
N	.621	.210	-.137	1.23
N	.610	.237	-.068	1.09
N	.599	.266	.002	1.66
N	.993	.001	.368	1.23
N	.831	-.005	.412	3.41
N	.685	-.011	.449	4.15
N	.378	.014	.249	1.75
N	.524	-.047	.249	1.00
N	.670	-.110	.249	2.91
N	.975	.006	.121	3.75
N	.835	.003	.087	1.04
N	.677	.000	.049	0.20

(7) L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 13 (1937).

N-N distances. However, it is not possible to determine the direction of the covalent bonds, since the differences⁶ in the interatomic distances are not significant in most cases. This is so because the *x*-coordinates were not directly determined and also because the standard deviations of the remaining parameters are rather large. An accurate determination of bond distances will have to wait until three-dimensional neutron data can be obtained.

Acknowledgment.—Thanks are due to Dr. J. V. R. Kaufman for bringing this problem to my attention and to Mr. I. Kluger for performing all the computer calculations. The author also is grateful to Dr. H. Danner, Brookhaven National Laboratory, for the neutron data and for the information on the work done at Pennsylvania State University.

(8) The Atlantic Refining Company, Philadelphia, Pa.

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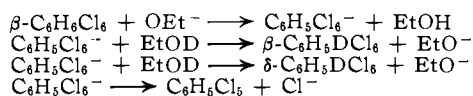
G. L. GLEN⁸

RECEIVED JUNE 1, 1963

The Mechanism of the Dehydrochlorination of β -Benzene Hexachloride¹

Sir:

Cristol proposed that the marked unreactivity of the β -isomer of benzene hexachloride (relative to that of the other isomers) is due to the absence, in that and only that isomer, of hydrogen and chlorine atoms *trans* to each other and on adjacent carbon atoms.² Although this proposal seems generally accepted, there is less agreement concerning the mechanism of the *cis*-dehydrochlorination of β -benzene hexachloride. Cristol and Fix³ pointed out that in a deuterated solvent the intermediate carbanion suggested for the reaction could either be deuterated with retention of configuration to yield labeled starting material, be deuterated with inversion of configuration to give labeled δ -benzene hexachloride, or lose a chloride ion to give a pentachlorocyclohexene. Either the δ -isomer or the pentachlorocyclohexene would then be rapidly dehydrochlorinated to a mixture of trichlorobenzenes.



As evidence for the intermediacy of a carbanion, Cristol and Fix reported 0.08% deuterium present in the β -benzene hexachloride isolated after about 50% dehydrohalogenation in 70% EtOD–30% EtOH.

Cram has stated that the most probable path of decomposition of the carbanion is *via* the formation of δ -benzene hexachloride, *cis* elimination from the carbanion being improbable, and that deuterated trichlorobenzenes should be produced in a deuterated solvent, since the deuterium atom of any intermediate δ -benzene hexachloride could be removed in a *trans* elimination only *via* a conformation with five axial chlorine atoms.⁴

In relation to our interest in the carbanion mechanism for β -elimination reactions,¹ we have examined the trichlorobenzene mixture produced in deuterated methanol.⁵ When 2.19 mmoles of β -benzene hexa-

chloride was 70% dehydrohalogenated by 6.9 mmoles of sodium methoxide in 98% MeOD–2% MeOH, the trichlorobenzene mixture (containing 88% of the 1,2,4-isomer) produced had n.m.r. and infrared spectra almost identical with those of the trichlorobenzene mixture produced under very similar conditions in "light" methanol. From blank experiments we conclude that $3.1 \pm 1.0\%$ 1,2,4-trichlorobenzene-3-*d* and much less of any other deuterated trichlorobenzene were present in the products of reaction in MeOD. Determination of the rate constant for the dehydrochlorination of β -benzene hexachloride in methanol and comparison with that for the exchange of 1,2,4-trichlorobenzene-3-*d*^{1b} showed that between 1 and 5%⁶ of the 1,2,4-trichlorobenzene produced in the reaction in MeOD would have been transformed to 1,2,4-trichlorobenzene-3-*d*.

We therefore conclude that if the alkaline dehydrochlorination of β -benzene hexachloride is initiated to any major extent by carbanion formation, the intermediate carbanions almost always lose chloride ions and are only rarely reprotonated. The possibility that the reaction proceeds only to a minor extent *via* intermediate carbanions but consists largely of a concerted *cis* elimination from a conformation, like the boat form, in which the dihedral angle between the hydrogen and chlorine atoms being removed is quite small⁷ has not been ruled out. However, in view of the slow rate of such *cis* eliminations⁸ and the added energy that would be required in the present case to reach such a conformation, the dehydrohalogenation of β -benzene hexachloride seems surprisingly fast to be a reaction of this type.

Acknowledgment.—We wish to thank the National Science Foundation for partial support of this investigation.

It seems that intermediate carbanions should be captured more efficiently in this solvent than in ethanol. If k_H/k_D is 5.0, 9% of the captured intermediates will escape deuteration in 98% MeOD but 68% will in 70% EtOD.

(6) Assuming that k_H/k_D is between 1 and 5.

(7) Cf. C. H. DePuy, R. D. Thurn, and G. F. Morris, *J. Am. Chem. Soc.*, **84**, 1314 (1962).

(8) Some of the data of Cristol and co-workers⁹ provide maximum values for the rates of such processes.

(9) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, **74**, 2193 (1952); S. J. Cristol and E. F. Hoegger, *ibid.*, **79**, 3438 (1957).

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RECEIVED OCTOBER 28, 1963

Photochemical and Thermal Rearrangement of α,β -Epoxyketones

Sir:

Investigations during the past decade have revealed the carbonyl group as an important and versatile chromophore in photochemical reactions.^{1,2} In view of the many acid- and base-catalyzed rearrangements exhibited by α,β -epoxyketones,³ it is surprising that the photochemical behavior of these substrates has not been widely studied.⁴ A recent investigation⁵ of the photolysis of some steroidal epoxyketones represents the only published case in which skeletal rearrangement occurs. We take this opportunity to report⁶

(1) P. de Mayo, *Advan. Org. Chem.*, **2**, 367 (1960).

(2) P. de Mayo and S. T. Reid, *Quart. Rev. (London)*, **15**, 393 (1961).

(3) R. Parker and N. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(4) The first of a few recent endeavors is that by H. E. Zimmerman, Abstracts of the Seventeenth National Organic Chemistry Symposium, June, 1961, Bloomington, Indiana, p. 31.

(5) C. Lehmann, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **45**, 1031 (1962).

(6) Part of this work was presented by W. Reusch and C. K. Johnson,

(1) (a) Part V in the series "The Carbanion Mechanism for β -Elimination Reactions"; (b) for part IV see J. Hine and P. B. Langford, *J. Org. Chem.*, **27**, 4149 (1962).

(2) S. J. Cristol, *J. Am. Chem. Soc.*, **69**, 338 (1947); cf. S. J. Cristol, N. L. Hause, and J. S. Meek, *ibid.*, **73**, 674 (1951).

(3) S. J. Cristol and D. D. Fix, *ibid.*, **75**, 2647 (1953).

(4) D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 321.

(5) In view of the greater acidity and ion-solvating power of methanol