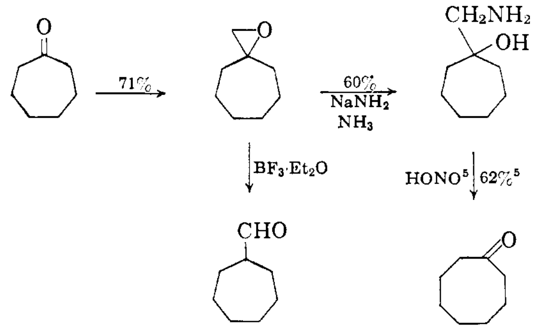
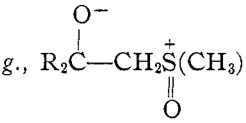
It is clear that at least in certain instances the reaction of II with a ketone is the most practical method for synthesis of the corresponding epoxide and that this, in turn, provides useful routes to other structures. For example, these transformations have now been established from cycloheptanone (yields given are probably not optimal)



91% (as 2,4-dinitrophenylhydrazone)

A different mode of reaction results in systems which are susceptible to Michael addition as illustrated by benzalacetophenone which reacts with II to form 1-phenyl-2-benzoylcyclopropane[6] (95% yield) and only minor amounts of the epoxide derived from carbonyl addition. Such reactions represent a promising method for carbocycle synthesis.

The methylide II probably is an intermediate in the base-catalyzed hydrogen–deuterium exchange previously observed[7,8] with I iodide. The fast rate of this exchange[7] and our own observations indicate that the ylide is quite stable; we are now engaged in chemical and physical studies aimed at defining the structure of sulfoxonium ylides and their reactivity in more detail. Whether methylene transfer from dimethylsulfoxonium methylide to unsaturated linkages occurs *via* an intermediate addition product, *e.g.*,  $R_2\overset{\overset{O^-}{|}}{C}—CH_2\underset{\underset{O}{\|}}{\overset{+}{S}}(CH_3)_2$, or by a direct route is not known at present. This point is also under investigation.

This work was supported by a grant from the National Institutes of Health.

(5) F. F. Blicke, J. Azura, N. J. Doorenbos and E. B. Hotelling, *J. Am. Chem. Soc.*, **75**, 5418 (1953).

(6) R. J. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957).

(7) S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).

(8) F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959).

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

E. J. COREY
MICHAEL CHAYKOVSKY

RECEIVED JANUARY 8, 1962

ON THE TWO FORMS OF HYDROGEN ATOMS IN NEUTRAL SOLUTIONS IRRADIATED BY X-RAYS

Sir:

Recently, data have been obtained[1-8] which indicate that most of the "H" atoms produced in irradiated aqueous neutral solutions are probably electrons. The results of Allan and Scholes[2] indicate that H atoms are produced in irradiated solutions by:

$$e_{aq} + H_3O^+ \longrightarrow H + H_2O \qquad (1)$$

and react with organic scavengers (*e.g.*, 2-propanol)

$$H + RH_2 \longrightarrow H_2 + RH \qquad (2)$$

However, even when all the electrons were scavenged by acetone, a residual yield of $G_{\text{hydrogen}} = 1.05$ was obtained.[2] This exceeds the "molecular" hydrogen yield by approximately $G = 0.6$, and was attributed to the formation of H atoms by excitation processes such as

$$H_2O^* \longrightarrow H + OH \qquad (3)$$

These results are in disagreement with those obtained in the H_2O_2–O_2,[7] methanol–azide[8] and 2-propanol-azide[8] systems, where only 0.0–0.3 H atoms as such were found to react at neutral pH's.

We used bicarbonate as an electron scavenger in neutral aqueous solutions. Neutral solutions of methanol, glucose, glycerol and acetate were irradiated by 200 kV. X-rays. In all these cases, 5×10^{-2} *M* bicarbonate was sufficient to reduce the hydrogen yield to about 1.05, although higher yields were obtained in some cases, when no bicarbonate was used (Table I). These results confirm the recent observations of Allan, *et al.*[6] However, in all the systems studied by us a constant limiting value of $G_{\text{hydrogen}} = 1.05 \pm 0.04$ is obtained.

Similar results were obtained by using acetone as an electron scavenger.

TABLE I

HYDROGEN YIELDS FROM AQUEOUS SOLUTIONS CONTAINING BICARBONATE AND ORGANIC SOLUTES; DOSE RATE 1000 PER MINUTE

Solute	Concn. in *M*	G_{hydrogen}	G_{hydrogen} in the presence of 0.05*M* bicarbonate	Total dose
Glucose	10^{-2}	1.50	1.03	2000
Glycerol	10^{-2}	1.16	1.09	2000
Methanol	10^{-1}	1.85	1.07	2000
Acetate	10^{-1}	1.25	1.01	2000

Using formate (0.047 *M*) and 2-propanol (0.01 *M*) about 2×10^{-4} *M* acetone was sufficient to reduce the hydrogen yield to about 1.1. When no acetone was added, H_2 yields were much higher (about 2) at the low doses used (1000*r*).

The higher hydrogen yields obtained in the absence of an efficient electron scavenger are in agreement with previous work[9,10] and probably are due to recombination of e_{aq} or its reaction with water.

---

(1) J. H. Baxendale and G. Hughes, *Z. physik. Chem.*, **14**, 323 (1958).

(2) J. T. Allan and G. Scholes, *Nature*, **187**, 218 (1960).

(3) N. F. Barr and A. O. Allen, *J. Phys. Chem.*, **63**, 928 (1959).

(4) G. Czapski, J. Jortner and G. Stein, *ibid.*, **65**, 964 (1961).

(5) E. Hayon and J. Weiss, Proc. 2nd Int. Conf. Peaceful Uses of Atomic Energy, Geneva, **29**, 80 (1958).

(6) J. T. Allan, N. Getoff, H. P., Lehmann, K. E. Nixon, G. Scholes and M. Simic, *J. Inorg. Nucl. Chem.*, **19**, 204 (1961).

(7) G. Czapski and A. O. Allen, in press, BNL Report, 5576.

(8) P. Kelly and M. Smith, *J. Chem. Soc.*, 1487 (1961).

(9) H. Fricke, E. J. Hart and H. P. Smith, *J. Chem. Phys.*, **6**, 229 (1938).

(10) S. Gordon and E. J. Hart, *J. Am. Chem. Soc.*, **77**, 3981 (1955).

TABLE II

k_4/k_2 IN NEUTRAL AND ACID SOLUTIONS.

Dose rate 1000 was r. min.$^{-1}$; total dose was 4000 r.

Solute and its concn. M		$C_{Fe(CN)_6^{-3}}$, M	Neutral solutions Electron scavenger present M	$G_{hydrogen}$	k_4/k_2	Acid solution k_4/k_2[12]
Glucose	0.01	1.5×10^{-4}	0.05 bicarbonate	0.71	108	100
Glucose	.01	8×10^{-5}[a]	0.05 bicarbonate	.86	75	
Glycerol	.01	7.5×10^{-5}[a]	0.05 bicarbonate	.80	128	200
Methanol	.10	6.2×10^{-5}[a]	0.05 bicarbonate	.81	1500	2350
2-Propanol[b]	.05	9.3×10^{-4}	9.3×10^{-4} ferricyanide	.82	39	77
Formate	.047	3.14×10^{-3}	2×10^{-4} acetone	.75	18	15.4

[a] Corrections have been made for the amount of ferricyanide which disappears during the irradiation. [b] In the presence of 10^{-4} M Na_2HPO_4.

These reactions of e_{aq} to produce H_2 as a final product in neutral solutions are relatively slow. Thus, minute quantities of electron scavengers which may be impurities, or products of irradiation will influence the values of $G_{hydrogen}$ when $G_{hydrogen} > 1.1$. The hydrogen yields obtained in the absence of an appropriate electron scavenger have no quantitative meaning.

When a sufficient amount of an electron scavenger is present, the hydrogen yield equals the sum of $G_{H_2} + G_3$ (where G_{H_2} denotes the so called "molecular" yield of hydrogen). G_3 seems to be constant and its value is 0.55 ± 0.05 in all the above systems, assuming $G_{H_2} = 0.5$. Since G_{H_2} may differ somewhat from this value and depend on the solute and on its concentration,[11] the sum of $G_{H_2} + G_3$ is expected to vary to the same extent.

To test whether the assumed reaction (3) really produces H atoms as such, competition between ferricyanide and RH_2 was carried out. Ferricyanide reacts with H atoms according to

$$H + Fe(CN)_6^{-3} \longrightarrow H^+ + Fe(CN)_6^{-4} \quad (4)$$

The yield of H_2 may be used to determine k_4/k_2, at neutral pH.

In Table II we compare the k_4/k_2 values, obtained by the competition of ferricyanide and RH_2 for H atoms produced in neutral solutions in the presence of a sufficient amount of an electron scavenger, to those obtained for acid solutions.[12]

The $G_{hydrogen}$ values are accurate to $\pm 5\%$. The values of k_4/k_2 were calculated assuming that $G_{H_2} = 0.5$ in all cases. From this $G_3 = 0.55$ results.

The agreement between the acid and neutral k_4/k_2 values confirms that at neutral pH the acid form of H atoms is produced by a mechanism which does not involve reactions of the neutral form of the reducing radicals in the bulk.

At present we have no explanation for the results[7,8] in systems where $G_3 \leq 0.30$. However, in our systems, the measure of G_3 is direct, the only assumption being the value of the "molecular" hydrogen yield.

The author is indebted to Prof. G. Stein for valuable comments.

DEPARTMENT OF PHYSICAL CHEMISTRY
THE HEBREW UNIVERSITY OF JERUSALEM
JERUSALEM, ISRAEL JOSEPH RABANI

RECEIVED DECEMBER 6, 1961

---

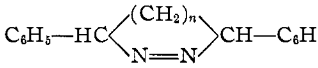
[11] H. A. Schwarz, *J. Am. Chem. Soc.*, **77**, 4960 (1955).

[12] J. Rabani, *J. Phys. Chem.*, **65**, 361 (1961).

A FIVE-MEMBERED RING AZO COMPOUND. A STEREOSELECTIVE DECOMPOSITION

Sir:

Recently increased impetus has been given to the question of whether or not biradicals couple with retention of configuration. Overberger and co-workers[1,2] have studied the decomposition of the seven- and eight-membered ring azo compounds of type I. One isomer of the seven-


I

membered ring azo compound (I, $n = 3$) was decomposed at 80 and 100° to give 1,5-diphenyl-1-pentene and a mixture of *cis*- and *trans*-1,2-diphenylcyclopentanes. One isomer of the eight-membered ring azo compound (I, $n = 4$) required somewhat higher temperatures (about 145°) but again, the corresponding olefin and a mixture of *cis*- and *trans*-1,2-diphenylcyclohexanes were obtained. Rinehart and Van Auken[3] have shown that at low temperatures, the photolysis of 3-carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline and of 3-carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline gave the corresponding cyclopropanes with retained configuration. Jones[4] also has studied the stereochemistry of the decomposition of 2-pyrazolines and found that the configuration of the resulting cyclopropanes does not depend upon their stability but rather upon the configuration of the intermediate 1-pyrazolines.

We wish now to report the synthesis and the stereospecific decomposition of the five-membered ring azo compound 3,5-diphenyl-1-pyrazoline (Ia), an analog of I ($n = 1$). Compound Ia was prepared by the addition of styrene to phenyldiazomethane. It is a white crystalline solid, m.p. 109–110° (dec.), λ_{max}^{EtOH} 329 mμ, ϵ_{max} 291.

Anal. Calcd. for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35. Found: C, 81.04; H, 6.28.

Two products could arise from the addition of styrene to phenyldiazomethane. Evidence for structure Ia was obtained as described.

---

[1] C. G. Overberger and J. G. Lombardino, *J. Am. Chem. Soc.*, **80**, 2317 (1958).

[2] C. G. Overberger and I. Tashlick, *ibid.*, **81**, 217 (1959).

[3] K. L. Rinehart and T. V. Van Auken, *ibid.*, **82**, 5251 (1960).

[4] W. M. Jones, *ibid.*, **82**, 3136 (1960).