

TABLE I  
ULTRAVIOLET SPECTRA OF CYCLOBUTANES I-V

	Isooctane		Ethanol		Acetonitrile	
	$\lambda_{\max}$ m $\mu$	$\epsilon$	$\lambda_{\max}$ m $\mu$	$\epsilon$	$\lambda_{\max}$ m $\mu$	$\epsilon$
I <sup>a</sup>	227	168	227	173		
	302	32.4	302	30		
	308	39.4	307	30		
II					232	30,000
					239	26,900
III	236	11,000	237	10,450	237	11,000
	319	120.5	318	120.5	316	120
IV			228	11,600		
			240	7,360		
			275	643		
V			223	207		
			290	30		

(a) The dione I shows additional absorption at 271 ( $\epsilon = 10.2$ ), 282 ( $\epsilon = 25.4$ ), 296 ( $\epsilon = 28$ ), and 348 m $\mu$  ( $\epsilon = 18.4$ ) in isooctane and at 282 ( $\epsilon = 24$ ) and 345 m $\mu$  ( $\epsilon = 18$ ) in ethanol.

N<sub>2</sub>O: C, 70.18; H, 6.42; N, 14.89. Found: C, 70.24; H, 6.62; N, 14.80).

Evidence for the retention of the four-membered ring in both II and III was afforded by the chemical analyses, as well as by the presence of a single peak in the proton n.m.r. spectra;  $\tau$  values<sup>4</sup>: I, 8.69; II, 8.24; III, 8.49.

Upon treating compound II with methyltriphenylphosphonium iodide or triethylamine, a remarkable rearrangement leading to formal exchange of two cyano groups with two methyl groups was observed to yield an isomeric product identified as IV, m.p. 158–159; (*Anal.* Calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>4</sub>: C, 71.17; H, 5.12; N, 23.71; mol. wt., 236. Found: C, 70.70; H, 5.22; N, 23.83; mol. wt., 245). The structure assignment of IV is based on (a)  $\lambda_{\max}^{\text{KBr}}$  4.45  $\mu$  (CN), 5.98  $\mu$  (isopropylidene group), 6.08  $\mu$  (C=C(CN)<sub>2</sub>), 7.16  $\mu$  and 7.28  $\mu$  (*gem* dimethyl); (b) the proton n.m.r. spectrum of CDCl<sub>3</sub> solution shows signals at  $\tau^4 = 7.82$ , 7.96, and 8.37 in a 1:1:2 intensity ratio in accord with the two different (isopropylidene) and two similar (ring *gem* dimethyl) methyl groups; (c) ozonolysis gave acetone, which was identified as the 2,4-dinitrophenylhydrazone derivative; (d) in tetrahydrofuran solution the product gave no e.p.r. signal at 25 or 50°. A nucleophile-catalyzed ring opening-ring closure sequence is proposed for conversion of II to IV.

The cyclobutanone V was prepared by acidification of the salt obtained in 60% yield by reaction of the cyclobutanone (III) with tetraethylammonium cyanide. Compound V has m.p. 155.5–156.5° (dec.);  $\lambda_{\max}^{\text{KBr}}$  4.45, 5.55, 7.2 and 7.25  $\mu$ ; (*Anal.* Calcd. for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O: C, 66.95; H, 6.08; N, 19.53. Found: C, 66.89; H, 5.99; N, 19.40).

The existence of non-bonded interaction of the  $\pi$ -orbitals at the 1,3 positions of compounds I–IV is suggested from the ultraviolet absorption data summarized in Table I.

For compound III the absorption at 237 m $\mu$  in ethanol is attributed to the dicyanomethylene group<sup>5</sup> and that at 318 m $\mu$  to the carbonyl group.<sup>6</sup>

(4) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(5) The wave length and intensity of this band is that expected for a cycloalkylenemalononitrile; e.g., cyclopentylidenemalononitrile has  $\lambda_{\max}^{\text{EtOH}}$  238.5 m $\mu$  ( $\epsilon$  12,000) (unpublished results of Dr. J. K. Williams).

With V as a model, the bathochromic shift of 28 m $\mu$  (290–318 m $\mu$ ) together with a four-fold increase in  $\epsilon$  is strongly indicative of interaction.

Transannular interaction in II causes the appearance of a doublet at 232 and 239 m $\mu$  with an  $\epsilon$  greater than the twofold increase expected from comparison with compound III. For IV, two new maxima appear at 228 and 275 m $\mu$ , in addition to the expected absorption at 240 m $\mu$  attributable to the dicyanomethylene function.

Evidence establishing 1,3-interaction in the dione I is less definitive. The spectra exhibit considerable fine structure. Assuming that the  $n \rightarrow \pi^*$  transition at 302–307 m $\mu$  corresponds to that at 290 m $\mu$  for V, a bathochromic shift in the range of 12–17 m $\mu$  is observed, however, without an increase in  $\epsilon$ . Whether this shift arises from intramolecular charge transfer<sup>7,8</sup> between the two carbonyl groups or whether, because of the known sensitivity of  $n \rightarrow \pi$  transition to polar environment,<sup>9</sup> it is due to the influence of the electrons of one carbonyl group on the  $n \rightarrow \pi$  transition<sup>10</sup> of the other is also unresolved.

These data will be discussed more fully in a forthcoming publication, and evidence will be presented indicating that 1,3-interactions of these compounds are not of significant importance in the ground state.

(6) The absorption in the 300 m $\mu$  region for compounds I and III is regarded as an  $n \rightarrow \pi^*$  transition of the carbonyl group since a hypsochromic shift is observed in changing to more polar solvents (see H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952), for leading references). These shifts are small in agreement with the observations of Kosower and Wu, who found that cyclobutanones give unusually low solvent-dependent shifts (E. M. Kosower and G.-S. Wu, *J. Am. Chem. Soc.*, **83**, 3142 (1961)).

(7) J. Tanaka and S. Nagakura, *J. Chem. Phys.*, **24**, 311 (1956).

(8) S. Nagakura, *ibid.*, **23**, 1441 (1955).

(9) L. Goodman and H. Shull, *ibid.*, **22**, 1138 (1954).

(10) H. L. McMurry, *ibid.*, **9**, 231 (1941).

CONTRIBUTION No. 717

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## THE REACTIVITY OF HYDROGEN ATOMS IN ALKALINE SOLUTIONS

Sir:

Recent radiation chemical investigations of aqueous solutions yield chemical evidence for the transient formation of  $e_{aq}$  (or H<sub>2</sub>O<sup>-</sup>), and the reactivity of this species with specific scavengers. The pH dependence, the effects of scavenger concentration and isotope effects in aqueous solutions of organic<sup>1,2</sup> and inorganic<sup>3–7</sup> solutes indicate that the entity  $e_{aq}$  is of considerable kinetic importance. The radiation stability of H<sub>2</sub>O<sub>2</sub><sup>3,4,8</sup> and N<sub>2</sub>O<sup>6,7</sup> in acid solutions is interpreted by assuming that these solutes act as efficient scavengers for solvated elec-

(1) D. Armstrong, E. Collinson, F. S. Dainton, D. M. Donaldson, E. Hayon, M. Miller and J. Weiss, *Proc. Int. Conference Peaceful Uses of Atomic Energy*, **29**, 80 (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**, 984 (1961).

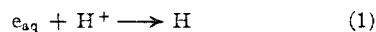
(5) A. R. Anderson and E. J. Hart, *ibid.*, **65**, 804 (1961).

(6) F. S. Dainton and D. B. Peterson, *Nature*, **186**, 878 (1960).

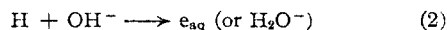
(7) G. Czapski and J. Jortner, *ibid.*, **188**, 4744 (1960).

(8) J. T. Sworski, *J. Am. Chem. Soc.*, **76**, 4687 (1954).

trons, while in acid solutions  $e_{aq}$  is converted to H atoms

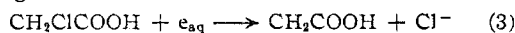


The conversion of H atoms to  $e_{aq}$  (or  $H_2O^-$ ) is of interest. An evidence for the reaction

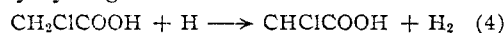


was obtained by the investigation of the reactivity of chloroacetic acid with atomic hydrogen in aqueous solutions.

The results of a radiation chemical investigation<sup>1</sup> of aqueous solutions of chloroacetic acid indicate<sup>1</sup> that this scavenger is an efficient electron acceptor leading to  $Cl^-$  formation



The reaction of H atoms in this system mainly proceeds by hydrogen abstraction



We investigated the reactivity of chloroacetic acid with H atoms generated in the gas phase and passed through the solution. Atomic hydrogen was generated by high frequency electrodeless discharge at 30 m.c. in  $H_2$  gas at 30 mm. pressure.<sup>9a</sup> The dose of atomic hydrogen was  $1.10^{-6}$  mole  $min^{-1}$  as determined by the ferricyanide dosimeter.<sup>9b</sup> The  $Cl^-$  ion formed was determined by a turbidimetric method. Blank experiments indicated that the hydrolysis of chloroacetic acid was negligible, and no  $Cl^-$  formation from the reaction products at pH 12.5 could be detected. Addition of 0.25 M  $Na_2CO_3$  had no effect on the chloride yield.

The experimental results for  $Cl^-$  production are expressed in terms of the reaction yield  $R$  defined as the number of  $Cl^-$  ions formed per H atom passed through the solution. Some experimental results are presented in Table I.

In the pH region 4–10  $R(Cl^-)$  was found to be independent of pH and of chloroacetic concentration in the region 0.05–0.5 M. These results indicate that the low value for  $R(Cl^-)$  obtained in the neutral region is a result of the efficiency of reaction 4. Chloride abstraction by H atoms from chloroacetic acid, present at this pH region as  $CH_2ClCOO^-$ , is less efficient by a factor of about 10 than the hydrogen abstraction reaction. These conclusions are in agreement with the results of Hayon and Weiss.<sup>1</sup> This comparative study of the reac-

(9) (a) G. Czapski and G. Stein, *J. Phys. Chem.*, **63**, 850 (1959); (b) G. Czapski and G. Stein, *ibid.*, **64**, 219 (1960).

TABLE I

$Cl^-$  yields from the decomposition of chloroacetic acid by H atoms at 4°: dose of H atoms  $1.10^{-6}$  mole  $min^{-1}$  duration of run 900 sec.; reproducibility  $\pm 20\%$ .

pH	$CH_2ClCOOH$ mole liter <sup>-1</sup>	$R(Cl^-)$
4.2	0.5	0.06
7.43	.01	.05
10.2	.01	.1
10.9	.01	.1
11.46	.01	.4
11.93	.01	.5
12.45	.01	1.0
12.6	.01	1.0
12.01	.5	0.07

tivity of H atoms produced in the gaseous phase and by ionizing radiations indicates again that the neutral H atom precursor in irradiated solutions is the solvated electron.

In alkaline solution at pH 11 a sharp rise of  $R(Cl^-)$  is observed reaching the limiting value of unity at pH 12.5. In the alkaline pH region the reaction yield increases with *decreasing* the scavenger concentration. These results can be interpreted by assuming the conversion of H atoms to  $e_{aq}$  (or  $H_2O^-$ ) by reaction 2. This species produces  $Cl^-$  by reaction 3. The concentration dependence is due to the competition between reaction 2 and 4.

The occurrence of reaction 2 was postulated previously.<sup>1,10,11</sup> However, the experimental evidence presented in the past in favor of this reaction can be interpreted satisfactorily by assuming the existence of  $e_{aq}$  as a primary product in irradiated solutions. The present experimental results yield a support in favor of the conversion of H atoms to solvated electrons or  $H_2O^-$  in alkaline solutions. The present experiments do not provide definite evidence proving the identity of  $e_{aq}$  the precursor of H atom in neutral solution, and the species formed from atomic H in alkaline solution.

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(11) J. G. Baxendale and G. Hughes, *Z. physik. Chem., N.F.*, **14**, 323 (1958).