

TABLE I  
ULTRAVIOLET SPECTRA OF CYCLOBUTANES I-V

|                | Isobutane                   |            | Ethanol                     |            | Acetonitrile                |            |
|----------------|-----------------------------|------------|-----------------------------|------------|-----------------------------|------------|
|                | $\lambda_{\max}$<br>m $\mu$ | $\epsilon$ | $\lambda_{\max}$<br>m $\mu$ | $\epsilon$ | $\lambda_{\max}$<br>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 isobutane 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 cycloalkyldienemalononitrile; e.g., cyclopentylidene-malononitrile 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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RECEIVED SEPTEMBER 27, 1961

#### THE REACTIVITY OF HYDROGEN ATOMS IN ALKALINE SOLUTIONS

Sir:

Recent radiation chemical investigations of aqueous solutions yield chemical evidence for the transient formation of  $e_{\text{aq}}$  (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  $e_{\text{aq}}$  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).

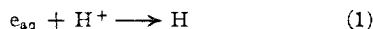
(5) A. R. Anderson and E. J. Hart, *ibid.*, **65**, 804 (1961).

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

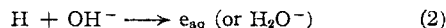
(7) G. Czapski and J. Jortner, *ibid.*, **188**, 4744 (1960).

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

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

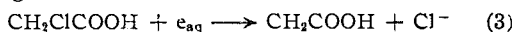


The conversion of H atoms to  $e_{aq}$  (or  $H_2O^-$ ) is of interest. An evidence for the reaction

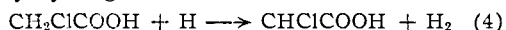


was obtained by the investigation of the reactivity of chloroacetic acid with atomic hydrogen in aqueous solutions.

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    | $CH_2ClCOOH$<br>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.

**Acknowledgment.**—We wish to thank Professor G. Stein for valuable comments.

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RECEIVED AUGUST 29, 1961

(10) H. L. Friedman and A. H. Zeltman, *J. Chem. Phys.*, **28**, 878 (1959).

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