

mately 0.1 Å shorter than in an octahedral complex. While the trend is in the correct direction, any further comparisons are futile because of the lack of data. The axial nitrogen bonds are about 0.2 Å longer than the distances found in square-planar complexes. The lengthening of the axial bonds is typical of trigonal-bipyramidal structures although examples involving nickel are rare.

The three angles SA1-Ni-SB1 (106.4°), SA1-Ni-Cl2 (120.5°), and SB1-Ni-Cl2 (133.1°) are distorted from the ideal value of 120°. However, the three ligands and the nickel atom are coplanar. The NA1-Ni-NB1 angle of 176.0° is only slightly smaller than the ideal value of 180.0°. These distortions are much smaller than in the case of Ni(CN)<sub>5</sub><sup>3-</sup> which was reported by Raymond, Corfield, and Ibers.<sup>5</sup>

Since both a water molecule and a chloride ion are available to complete the octahedron, the question of the reason for the pentacoordination is puzzling. A survey of the known octahedral structures<sup>4</sup> indicates that S<sub>4</sub>Cl<sub>2</sub> and N<sub>2</sub>S<sub>4</sub> coordination about nickel is known. This observation suggests that either the methyl groups are providing steric hindrance or that the coordination is related to electronic effects of the ligand. Further preparative and structural studies of thiosemicarbazones with nickel and other metal salts are in progress to elucidate the factors involved in the formation of the trigonal-bipyramidal structure.

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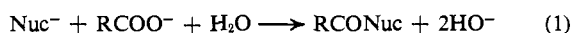
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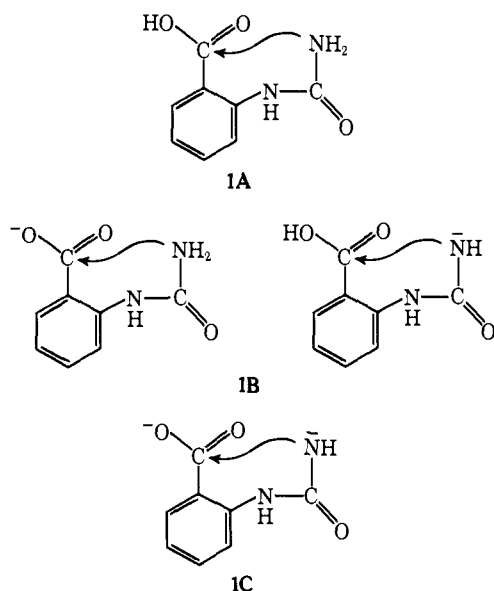
### Anionic Nucleophilic Attack upon a Carboxyl Anion

Sir:

We wish to report the first example of an anionic nucleophilic displacement upon a carboxyl anion (eq 1).



In our hands, N-(*o*-carboxyphenyl)urea (1) was found to cyclize in water to yield 2,4-dihydroxyquinazoline



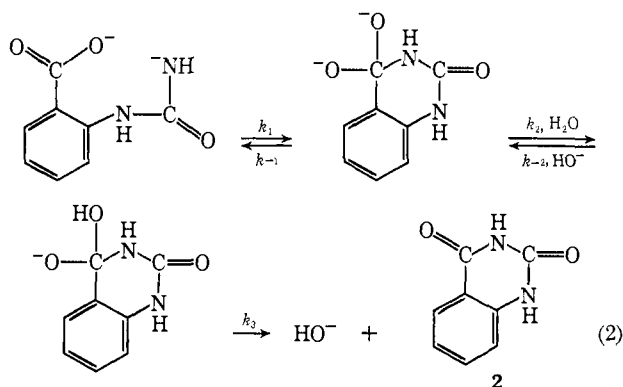
(2). Without invoking sound chemical reasoning the cyclization process could involve the species 1A, 1B, or 1C. *A priori*: (1) ring closure from 1A would not appear reasonable since the strong base HO<sup>-</sup> is expelled by the weakly basic ureido nitrogen; (2) the involvement of the two species of 1B cannot be differentiated kinetically; that involving attack of the weakly basic ureido nitrogen would appear impossible but displacement of HO<sup>-</sup> by the strongly basic ureido nitrogen anion would be the most reasonable of all the alternate mechanisms; and (3) attack of an anionic center upon a carboxyl anion as in 1C has no precedence in organic chemistry and would appear impossible. Mechanisms involving species 1A, 1B, and 1C may be kinetically differentiated. At pH values much greater than the pK<sub>a</sub> of the carboxyl group, the rate of reaction of 1A should decrease linearly with decrease in a<sub>H</sub>, the rate of reactions involving 1B should be insensitive to a<sub>H</sub>, while the rate of reaction of 1C should increase linearly with decreasing a<sub>H</sub>. The pseudo-first-order rate constants for the formation of 2 from 1 were found to increase linearly with decreasing a<sub>H</sub>.<sup>1</sup> In Table I are provided the pH values employed, the experimental values of k<sub>obsd</sub>, and the second-order rate constants calculated from the expression k<sub>2</sub>[1]·[HO<sup>-</sup>]. Examination of Table I reveals that k<sub>2</sub> remains

Table I. Pseudo-First-Order Rate Constants (k<sub>obsd</sub>) and Calculated Second-Order Rate Constants (k<sub>2</sub>) as a Function of pH

pH	10 <sup>4</sup> k <sub>obsd</sub> , sec <sup>-1</sup>	10 <sup>4</sup> k <sub>2</sub> , l. mol <sup>-1</sup> sec <sup>-1</sup>
13.70	410	5.56
13.01	85	5.66
12.61	34	5.66
11.34	1.7	5.42

constant, within experimental error, over greater than a 100-fold change in a<sub>H</sub>.

To obviate expulsion of O<sup>2-</sup> from 1C one of several plausible mechanisms would be that of eq 2, with k<sub>1</sub> rate determining.



(1) Rate determinations were carried out at 30°, μ = 1.0 with KCl in the absence of buffer by employing a special spectrophotometric titration cell attached to a Cary 15 recording spectrophotometer and a Radiometer pH-stat assembly. The product 2 was identified at the end of selected kinetic runs by spectrophotometric titration in the reaction cell (pK<sub>a</sub> = 9.60). The pK<sub>a</sub> of an authentic sample of 2 (N. A. Lange and F. E. Sheibley, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 79) was determined to be 9.60 (NH function between the two C=O groups). Ultraviolet spectra of product and authentic 2 are identical at varying pH values.

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### Photolysis of 1,4-Dichlorobutane Sensitized by the $n, \pi^*$ Singlet State of Acetone

Sir:

We wish to report the photodecomposition of 1,4-dichlorobutane (1,4-DCB) sensitized by the  $[n, \pi^*]^1$  state of acetone, a reaction that may be the first example in which this particular state photosensitizes a chemical, rather than a physical, process. Although much interest has been shown in photosensitization of the  $[n, \pi^*]^3$  state of acetone and other carbonyl compounds,<sup>1-6</sup> apparently the only cases of photosensitization by the corresponding  $[n, \pi^*]^1$  state involve sensitization of biacetyl fluorescence,<sup>7</sup> or quenching of type II photoelimination from aliphatic ketones,<sup>8</sup> through singlet-singlet energy transfer to biacetyl. The acetone photosensitized decomposition of 1,4-DCB is of added interest since it offers photochemical indications for the occurrence of excimer and monomer forms of the  $[n, \pi^*]^1$  state, complementing recently reported photochemical evidence, based on fluorescence measurements.<sup>9</sup>

Degassed 1,4-DCB-acetone solutions, with and without isooctane as inert diluent, were sealed in tubes with optically flat quartz or Pyrex windows and irradiated at 3130 Å in a merry-go-round apparatus.<sup>10</sup> The major products were hydrogen chloride and 1,3-dichlorobutane (1,3-DCB). This communication is concerned only with the former product, and detailed results will be presented later.<sup>11</sup> The initial quantum yields for HCl formation<sup>12</sup> ( $\approx 1\%$  photolysis) are all acetone photosensitization values; the yields, for quartz tubes, represent only the energy-transfer contribution after subtracting the calculated contribution due to direct absorption by 1,4-DCB at 2537 Å<sup>13</sup> (using  $\Phi(\text{HCl}) = 0.032$  for the direct photolysis<sup>11</sup>). The data obtained with Pyrex and quartz<sup>14</sup> windows show that it is im-

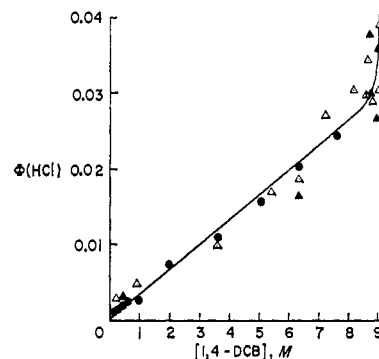


Figure 1. Effect of 1,4-dichlorobutane concentration on the quantum yield of hydrogen chloride at 3130 Å. The circles correspond to 1,4-DCB-acetone-isooctane solutions at constant acetone concentration (0.544 M), and the triangles correspond to 1,4-DCB in acetone alone. The open symbols denote runs in quartz tubes and the closed symbols denote those in Pyrex;  $\Delta$  represents a typical run in quartz at 2537 Å.

material if the radiation is  $\approx 3100$  Å, so long as it lies within the acetone  $n \rightarrow \pi^*$  band. This implied wavelength independence of  $\Phi(\text{HCl})$  was confirmed by runs in quartz tubes using monochromatic 2537-Å radiation.<sup>15</sup>

Figure 1 shows  $\Phi(\text{HCl})$  to be essentially a linear function of 1,4-DCB concentration over almost the entire concentration range. This is so whether the samples contain only 1,4-DCB and acetone, or contain a fixed acetone concentration in various 1,4-DCB-isooctane solutions. At the highest substrate concentrations (neat 1,4-DCB = 9.13 M), where [acetone]  $\approx 0.2$  M, there is a significant departure from a straight line because  $\Phi(\text{HCl})$  is then markedly dependent on acetone concentration (see Figure 2). The absence of a sharp rise in yield with leveling off at low substrate concentration, characteristic of triplet-triplet energy transfer (e.g., acetone<sup>2,4</sup> or benzene<sup>16</sup> photosensitized *cis-trans* isomerization of an olefin), suggests that the  $[n, \pi^*]^3$  state is not involved here. This view is supported by the fact that irradiation in the presence of dissolved oxygen, or a simple olefin, both efficient triplet quenchers,<sup>4</sup> did not suppress the photosensitized reaction. Furthermore, although the benzene triplet sensitizes the photolysis (and radiolysis) of chloroform<sup>17,18</sup> or carbon tetrachloride,<sup>17</sup> triplet sensitization of the radiolysis<sup>17</sup> of ethyl and propyl chlorides is not observed; hence, it probably does not occur in the photolysis of 1,4-DCB either. On the other hand, quenching of acetone fluorescence (at 340 m $\mu$ ) by 1,4-DCB, though inefficient, was definitely observed, with a Stern-Volmer plot showing a slight upward curvature and an initial slope of  $\sim 0.05$  M<sup>-1</sup>. These facts all indicate that the  $[n, \pi^*]^1$  state of acetone is the probable source for the photosensitized decomposition of 1,4-DCB. The possibility that acetone sensitization in-

(14) The quartz windows were used to enhance acetone absorption at  $\sim 2850$  Å, thereby increasing the likelihood of observing effects from the monomer form of the  $[n, \pi^*]^1$  state, as opposed to the excimer.<sup>9</sup>

(15) The Rayonet reactor<sup>10</sup> equipped with low-pressure mercury resonance lamps.

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(9) M. O'Sullivan and A. C. Testa, *ibid.*, **90**, 6245 (1968); their findings have been verified by the present author.

(10) Rayonet reactor, equipped with 16 fluorescent lamps with emission peaked at 3130 Å, and calibrated with uranyl oxalate actinometry. The tubes had a 4-mm light path, and the absorption properties of the solutions were calculated from measured uv spectra.

(11) M. A. Golub, submitted for publication.

(12) Potentiometric titration with NaOH of methanol-water extracts of the frozen contents of irradiated tubes.

(13) Although most of the emission from this source<sup>10</sup> is centered at 3130 Å,  $\sim 15\%$  is at 2537 Å.