

of a reaction intermediate, since the addition of enough sodium acetate to ensure at least a doubling of acetate ion concentration leads to no change in product composition.

The composition of the inverted product could be accounted for by a proton abstraction from the diazonium ion by the internal acetate ion of III to form a diazoalkane, which could react fairly stereospecifically with acetic acid (but not with water) to form the more stable, inverted acetate. However, this is ruled out by the finding that the α -deuteriodecalylamine gives about the same product composition as the protium compound.¹³

The explanation for the failure of the more nucleophilic water molecules to attack the cationic intermediates more readily than do acetic acid molecules is probably related to the great nonselectivity of the intermediate "hot" carbonium ion.¹⁴ It also appears likely, in accord with the views of other workers,^{6,11} that substantial nucleophilic participation by solvent in the loss of nitrogen does not occur, since water should be much more effective than acetic acid in this process.

These results also provide a partial explanation for the much greater degree of retention observed upon the deamination of 5α -cholestan- 3α -ylamine in 23 mole %¹⁵ acetic acid in water³ than in the deamination of I in 3.4 mole %¹⁵ acetic acid.⁴ For reasons as yet unknown, the degree of inversion increases sharply with water content in the more aqueous solvents.

The technique used here appears to offer great promise as an informative probe in mechanistic studies of nitrous acid deaminations and, hopefully, of other solvolysis reactions.

(13) The isotope effect would be expected to reduce the importance of the diazoalkane path and to decrease the yield of inverted acetate.

(14) D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **79**, 2866 (1957).

(15) 23 mole % and 3.4 mole % correspond respectively to 30 and 10 volume %.

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Pulse Radiolysis of Gases¹

Sir:

The technique of pulse radiolysis^{2,3} has been used with considerable success to observe the optical absorption spectra of transient species and to determine the rate constants for elementary reactions in the radiolysis of liquid systems.⁴ We have now extended this technique to the study of gaseous systems. In the pulse radiolysis of rare gas-naphthalene systems, we have observed the triplet state of naphthalene. In a kinetic study of irradiated oxygen we have determined the absolute rate constant for the reaction of oxygen atoms with molecular oxygen to form ozone.

The general experimental technique is similar to that used for liquids and has been described in detail.³ In the present work, a stainless steel cell, permitting high pressures, was used with the 14-Mev. electron beam and pulses of 0.4 to 5 μ sec. The cell, 13 cm. in

inside length, had a front window of aluminum, 1 mm. thick. The rear window, through which the analyzing light beam passed, was of high purity silica, 0.5 in. thick. A thin mirror inside the cell at the front was used with either two or four reflections, giving a light path of 26 or 52 cm.

The naphthalene system irradiated consisted of 10 to 30 atm. of xenon and about 0.1 mm. of naphthalene. A transient absorption spectrum was observed, consisting of three bands centered at 3984, 3772, and 3430 Å., with half-widths of about 60–70 Å. and relative optical densities at the maxima of 1.0, 0.4, 0.15, respectively. This spectrum is assigned to the triplet state of naphthalene on the basis of the good agreement of the wave lengths, relative intensities, and half-widths of the bands with the three bands of greatest intensity observed by Porter⁵ in the flash photolysis of naphthalene vapor and assigned to the triplet state. Two weaker bands observed by Porter were not seen because of the low concentration of triplet.

Within our time resolution of about 0.5 μ sec., the naphthalene triplet seems to be formed instantaneously. There are several possible modes of formation of the triplet, one of the more likely of which is direct electron impact by subexcitation electrons⁶ in this two-component system.

The decay of the triplet was observed spectrophotometrically after the electron pulse by monitoring the bands at 3984 and 3772 Å. The decay appears not to follow a simple first- or second-order rate law. Under the conditions of the experiment, the decay had an approximate half-time of 3 to 6 μ sec. followed by a longer decay of 10 to 20 μ sec. The decay kinetics are being investigated.

The ozone formation reaction (eq. 1) was investi-



gated over an oxygen pressure range of 7 to 130 mm. with argon present at pressures up to 100 atm. The Ar, in these experiments, was taken as the third body, M. The reaction was monitored at 2600 Å. where the ozone has a suitable absorption band.⁷ The pulse duration was 0.4 and 1 μ sec. The formation rate curves obey a first-order rate law. These curves were generally analyzed starting at about 1.5 μ sec. after the electron pulse and had half-times of about 0.7 to 7 μ sec. The experimental results obtained, as well as calculations based on considerations of reactions of ionic and excited species likely to be responsible for the production of oxygen atoms, seem to indicate that the formation of oxygen atoms is negligible 1 μ sec. after the end of the pulse.

The data obtained give $k_1 = (0.7 \pm 0.3) \times 10^{14}$ (cc. mole⁻¹)² sec.⁻¹ at 25°. This value, obtained by a technique which is completely different from previous investigations, may be compared with recent values obtained in other ways. Measurements of ozone decomposition and equilibrium considerations,^{8–10}

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(6) R. L. Platzman, *Radiation Res.*, **2**, 1 (1955).

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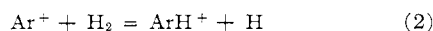
(3) L. M. Dorfman, I. A. Taub, and R. E. Bühler, *ibid.*, **36**, 3051 (1962).

(4) For a survey, see L. M. Dorfman, *Science*, **141**, No. 3580, 493 (1963).

taken together with the ratio^{11,12} $k_1^{\text{Ar}}/k_1^{\text{O}_2} \cong 0.6$, give $k_1 = 0.7$ to 1.0×10^{14} (cc. mole⁻¹)² sec.⁻¹. Recent direct measurements by Kaufman and Kelso¹² give $k_1 = 1.5 \times 10^{14}$ (cc. mole⁻¹)² sec.⁻¹ and by Clyne *et al.*,¹³ give $k_1 = 2.0 \times 10^{14}$ (cc. mole⁻¹)² sec.⁻¹. The value obtained in these preliminary pulse radiolysis investigations is in reasonable agreement.

Reaction 1 is also being studied in the system Ar-N₂O-O₂. The uncertainties are presently greater in this case, and a value for k_1 has not yet been determined. A complete account of all the work involving molecular oxygen will be presented in the near future.

The method offers considerable promise as a fast reaction technique for the investigation of atomic reactions in the gas phase. Thus, in a manner similar to the oxygen study, a microsecond burst of hydrogen atoms may be obtained by reaction 2 and the



subsequent kinetics followed where optically absorbing products are formed.

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Azo Coupling of Aryldiazonium and B₁₀H₁₀⁻² Ions

Sir:

Recent studies have shown the polyhedral B₁₀H₁₀⁻² ion to be a very reactive substrate in apparent electrophilic substitution reactions. Examples of halogenation,¹ alkylation,^{1a} nitrosation,² and deuteration³ have been presented. We wish to report the extremely facile azo coupling reaction which occurs between a variety of aryldiazonium ions and the B₁₀H₁₀⁻² ion. The resulting products are highly colored dyes formally related to the well-known azo dyes and as such are monosubstituted B₁₀H₁₀⁻² ions. Crystalline products have been isolated and characterized using unsubstituted, *p*-CH₃-, *p*-Br-, *p*-CH₃O-, *p*-NO₂-, *m*-NO₂-, *m*-CH₃O-, and *m*-CF₃-benzenediazonium tetrafluoroborates or hexafluorophosphates. In a typical preparation, 0.050 mole of *p*-BrC₆H₄N₂BF₄ dissolved in 50 ml. of acetonitrile was added to 0.050 mole of K₂B₁₀H₁₀ dissolved in 1 l. of acetonitrile at -35°. A yellow solution resulted which rapidly became purple. This solution was warmed to room temperature and concentrated to about 25 ml. *in vacuo*, whereupon 0.052 mole of KBF₄ was isolated by filtration. The filtrate was passed through a column of acid-washed alumina, concentrated to near dryness, and dissolved in dilute

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(2) W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muettterties, *J. Am. Chem. Soc.*, **86**, 115 (1964).

(3) E. L. Muettterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

aqueous mineral acid. The addition of an aqueous solution of tetramethylammonium chloride precipitated the tetramethylammonium salt of the monoprotated azo coupling product. *Anal.* Calcd. for C₁₀H₂₆N₃B₁₀Br: C, 31.90; H, 6.96; N, 11.16; B, 28.74; Br, 21.23; equiv. wt., 376. Found: C, 32.14; H, 7.05; N, 11.05; B, 28.60; Br, 21.20; equiv. wt., 370. When the precipitation with tetramethylammonium chloride was carried out in basic solution, the tetramethylammonium salt of the substituted B₁₀H₁₀⁻² ion was obtained. *Anal.* Calcd. for C₁₄H₃₇N₄B₁₀Br: C, 37.40; H, 8.30; N, 12.46; B, 24.07; Br, 17.78; equiv. wt., 450. Found: C, 37.14; H, 8.25; N, 12.16; B, 23.92; Br, 17.54; equiv. wt., 446.

Attempts to carry out the coupling reactions in aqueous solution led to the rapid precipitation of yellow solids upon mixing the two reactants. After isolation and drying, these yellow solids detonated with considerable brisance. At the present time these materials are considered to be water-insoluble aryldiazonium salts which contain the B₁₀H₁₀⁻² anion. When added to acetonitrile or acetone, these salts dissolved and generated the corresponding protonated azo coupling products which were isolated as their tetramethylammonium salts in the usual way.

The ArN=NB₁₀H₉⁻² species and their conjugate acids are reversibly interconverted by the addition of acid or base, respectively. The pK_A's associated with this acid-base equilibrium were determined for the eight available compounds by a spectrophotometric method in aqueous buffer solutions.⁴ A fairly linear function of the Hammett σ -constant was obtained from these data with a ρ -value of 1.7 for dissociation of the conjugate acids.

The ¹¹B n.m.r. spectra of the ArN=NB₁₀H₉⁻² species and their conjugate acids were obtained at 19.3 and 32 Mc./sec. In both series only apical substitution was observed. In the conjugate acid form, the additional proton is not coupled to the substituted boron atom. This, coupled with the similarity in the ρ -value determined in this study to the ρ -value obtained in the corresponding equilibria with monosubstituted azobenzenes⁵ (2.2) and with the similar shifts observed in the ultraviolet absorption spectra of azobenzene⁶ (321 to 420 m μ) and C₆H₅N=NB₁₀H₉⁻² (341 to 453 m μ) upon acidification, suggests that protonation of species of the latter type occurs on nitrogen. The greater basicity of ArN=NB₁₀H₉⁻² species relative to azobenzene (by about 8 pK units) is consistent with the enhanced basicity of B₁₀H₉N(CH₃)₂^{-2(1a)} relative to N,N-dimethylaniline.⁷

The coupling reaction is probably best described as an electrophilic substitution reaction on B₁₀H₁₀⁻² to form ArN=NB₁₀H₉⁻² and 1 equiv. of hydrogen ion followed by protonation of the coupling product. Of additional interest is the fact that the B₁₀H₁₀⁻² and B₁₀D₁₀⁻² ions show no kinetic isotope effect in a competitive coupling reaction with *p*-methoxybenzenediazonium ion. Apparently some step prior to B-H bond-

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