

that C<sub>8</sub> and C<sub>12</sub> compounds comprised all detectable products; no products between C<sub>8</sub> and C<sub>12</sub> were observed. Material balance calculations showed that the C<sub>8</sub> and C<sub>12</sub> compounds detected constituted over 95% of the reacted isobutylene. In several experiments the polarity of the electric field was reversed. With reversed polarity no products were observed; also, direct photolysis of isobutylene vapor at 5 torr produced no detectable C<sub>8</sub> or C<sub>12</sub> products. These results support our contention that the positive ions are reacting in the liquid phase.

The C<sub>8</sub> products were analyzed on a AgNO<sub>3</sub>-benzyl cyanide gas chromatographic column, which discriminates between alkenes and alkanes, and on an SE-30 column, which discriminates according to boiling point. The compounds were identified by retention-time comparison on both columns with C<sub>8</sub> standards from Chemical Samples Co., and identification was confirmed in part by mass spectrometry. Table I summarizes the products found at -128°; it will be seen that the individual C<sub>8</sub> isomers reveal the probable structure of the C<sub>8</sub> carbonium ions and how they are neutralized.

**Table I.** Relative Yields of C<sub>8</sub> and C<sub>12</sub> Products from *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> Reaction with Liquid Isobutylene<sup>a</sup>

Product	Yield, %
Relative Total Products	
C <sub>8</sub> products	73 ± 6
C <sub>12</sub> products	27 ± 4
Relative C <sub>8</sub> Products	
2,2,4-Trimethylpentane	4.5 ± 1.0
2,4,4-Trimethylpentene-2	48.4 ± 4.8
2,2,3-Trimethylpentane	19.8 ± 1.1
3,4,4-Trimethylpentene-2	27.3 ± 3.8

<sup>a</sup> 120-min photolysis, -128°.

The krypton resonance lamp emits photons at 1236 Å (10.0 eV) and 1165 Å (10.6 eV) with relative intensities of 1.00 and 0.28, respectively.<sup>6</sup> The ionization potential of isobutylene is 9.4 eV, and the lowest appearance potential for a fragment ion from isobutylene is 11.3 eV (C<sub>4</sub>H<sub>7</sub><sup>+</sup>).<sup>7</sup> Therefore the only ion produced is the parent C<sub>4</sub>H<sub>9</sub><sup>+</sup>. Under our experimental pressure (0.05 torr) and nominal electric field (70 v/cm), we calculate that the C<sub>4</sub>H<sub>9</sub><sup>+</sup> ion will make one or two collisions with isobutylene to form mainly *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> as shown by mass spectrometry<sup>8-10</sup> before reaching the liquid. The electron released may gain sufficient energy in the electric field to cause ionization and fragmentation. However, variation of the nominal electric field produces no change in product distribution, so such electron fragmentation does not seem to be significant. We conclude that most of the ions striking the liquid are *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> with some unreacted C<sub>4</sub>H<sub>8</sub><sup>+</sup> also present.

*t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> can react with the two double-bonded carbons in isobutylene. Reaction with the terminal carbon in isobutylene gives a 2,2,4-trimethylpentyl carbonium ion. This yields the correct carbon skeleton for the major product. There are two basic neutral-

ization reactions for the C<sub>8</sub> carbonium ions: one is hydride transfer to the carbonium ion to yield an alkane plus C<sub>4</sub>H<sub>7</sub><sup>+</sup>, and the other is proton transfer from the carbonium ion to give an alkene plus C<sub>4</sub>H<sub>9</sub><sup>+</sup>. Both the 2,2,4 alkene and alkane are observed, but their relative abundances show that proton transfer predominates by 10:1. This selectivity is probably associated with the stability of the product C<sub>4</sub>H<sub>9</sub><sup>+</sup>; it also demonstrates that we can obtain relative rates of ion-molecule reactions in certain liquids.

The other two C<sub>8</sub> products indicate somewhat surprisingly that *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> also reacts at the tertiary carbon in isobutylene. This yields a 2,2,3,3-tetramethylbutyl primary carbonium ion which is expected to rearrange rapidly to give the tertiary 2,2,3-trimethylpentyl structure. Proton transfer from and hydride transfer to this carbonium ion lead to the observed 3,4,4 alkene and 2,2,3 alkane, respectively. For this carbonium ion the results show that proton transfer again predominates, but only by 2:1.

It is interesting to point out that the total reactivity of *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> at both the primary and tertiary carbons in isobutylene is about 50%. Since *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> shows so little selectivity in this situation, it may well be excited. We are presently studying the effects of electric field and temperature to gain more insight into this possibility. We are also investigating other liquid-phase ion-molecule reactions by this new technique.

**Acknowledgment.** This research was generously supported by the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California.

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Received February 25, 1967

## Evidence for Trapped Dielectrons in Ice

Sir:

Electrons produced by  $\gamma$  radiation are trapped in hydroxide ices at 77°K. The trapped electron, e<sub>t</sub><sup>-</sup>, is characterized by an epr singlet at  $g = 2.001$ ,<sup>1</sup> a broad absorption band with a maximum at 5850 Å,<sup>2</sup> and a hydroxide anion vacancy trapping site.<sup>3</sup> We have found that at high radiation doses e<sub>t</sub><sup>-</sup> reacts to form a diamagnetic species which we believe to be best described as a dielectron, e<sub>2t</sub><sup>2-</sup>, or two electrons trapped in the same hydroxide anion vacancy.

Frozen solutions of 10.0 and 6.0 M NaOH were  $\gamma$  irradiated at 77°K with Co<sup>60</sup>. The yields of e<sub>t</sub><sup>-</sup> and O<sup>-</sup> were measured by epr under conditions where power saturation was absent. The results as a function of radiation dose are shown in Figure 1.

The e<sub>t</sub><sup>-</sup> yield saturates at about 2 Mrads in both 6 and 10 M NaOH, and the saturation yield in 6 M NaOH is proportionately less than in 10 M NaOH. The striking result is the decrease in the e<sub>t</sub><sup>-</sup> yield above 8 Mrads; the optical absorption band shows a similar decrease. Since the O<sup>-</sup> yield continues to increase over the entire dose range, and since no new para-

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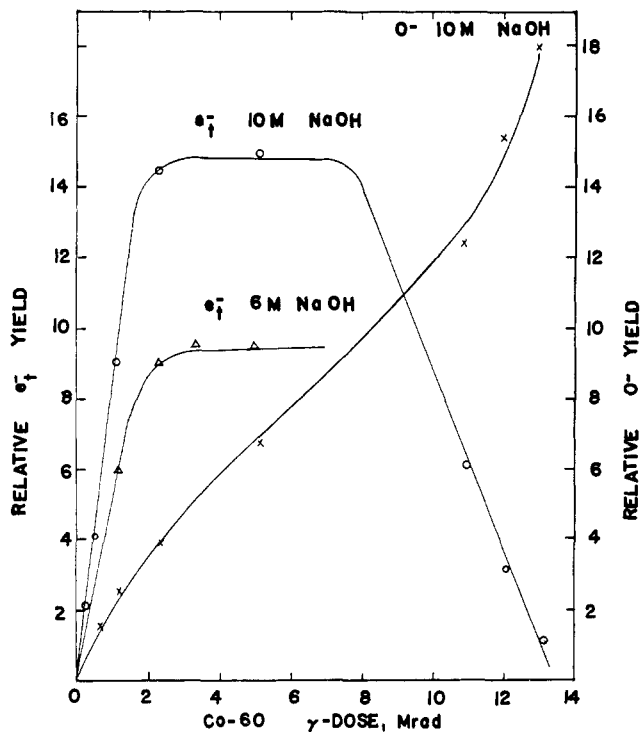
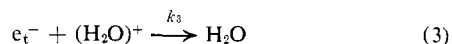
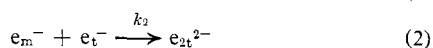


Figure 1. Relative  $e_t^-$  and  $O^-$  yields as a function of  $\gamma$  radiation dose in alkaline ices at 77°K.

magnetic species are observed, the  $e_t^-$  must react above 8 Mrads with a species other than  $O^-$  to form a diamagnetic species.

A plausible explanation for the dose saturation behavior is suggested by considering reactions which can compete with the trapping reaction for radiation-produced mobile electrons,  $e_m^-$ . The trapping reaction is shown by (1) where T denotes an available trap for  $e_m^-$ , and possible competing reactions for  $e_m^-$  are given by (2) and (3).



From the dose saturation data for 6 and 10 M NaOH, it is seen that the number of traps available in the system is proportional to  $[OH^-]$ . Reaction 3 involving the radiation-produced hole,  $(H_2O)^+$ , predicts that the dose saturation yield should be independent of  $[OH^-]$  and that the dose at which saturation occurs should depend on  $[OH^-]$ . Neither prediction is observed experimentally, so reaction 3 does not explain the results.

The formation of  $e_{2t}^{2-}$  by reaction 2 is consistent with our results. The onset of dose saturation occurs when a specific fraction of the available traps are filled; hence it is independent of  $[OH^-]$ . At low doses,  $k_1[T] \gg k_2[e_t^-]$ ; saturation occurs when  $k_1[T] = k_2[e_t^-]$ ; and for  $k_2 > k_1$ ,  $[e_t^-]$  decreases at high doses.

In an  $e_{2t}^{2-}$  center we expect that the second electron would be bound more weakly than the first electron. In this case thermal dissociation could lead to  $e_{2t}^{2-} \rightarrow e_t^-$ . We searched for this reaction by warming colorless spheres of 10 M NaOH that had been irradiated to 15 Mrads at 77°K and showed no epr spectrum due to

$e_t^-$ . Above 120°K a blue color was observed to appear; this was trapped by suddenly recooling to 77°K. Both the epr line and optical band of  $e_t^-$  were then observed for the warmed samples. We believe this experiment conclusively demonstrates the existence of  $e_{2t}^{2-}$ .

The direct analogy of  $e_{2t}^{2-}$  in hydroxide ices is the F' center in irradiated alkali halides.<sup>4</sup> The F' center consists of two electrons trapped in the same halide ion vacancy; it is diamagnetic, has broad optical absorption in the near-infrared, can be thermally dissociated to yield the F center which is analogous to  $e_t^-$ , and can be produced by optical bleaching of the F center. Symons and co-workers<sup>5</sup> have studied optical bleaching of  $e_t^-$  and indeed find a new, broad absorption in the near-infrared, although no maximum could be observed. This observation is additional evidence for  $e_{2t}^{2-}$ .

The binding of two electrons in the same anion vacancy can be understood qualitatively as follows. The wave function of  $e_t^-$  extends over a greater volume than that of the  $OH^-$  which it replaces; consequently, there will be a small potential well in the  $e_t^-$  volume which can bind a second electron. This argument implies that the second electron is bound more weakly than the first. Vinetskii and Giterman<sup>6</sup> have calculated the interaction of two electron centers in a dielectric medium. They find a minimum in the potential curve at an  $\sim 4$ -Å separation between the two electrons. The radius of the  $e_t^-$  charge distribution has been previously estimated as 3–4 Å from experimental data.<sup>3</sup> Hence the existence of  $e_{2t}^{2-}$  seems compatible with the approximate theoretical calculations.

**Acknowledgment.** This research was generously supported by the Air Force Rocket Propulsion Laboratory and the U. S. Atomic Energy Commission. This is AEC Document No. COO-1528-11. J. Z. is grateful to the U. S. Atomic Energy Commission for an Advanced Health Physics Fellowship and to Professor F. E. Hoecker for his cooperation. We thank Professor R. N. Adams for making available the epr equipment and Professor R. Friauf and D. Renneke for helpful discussions.

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Received March 20, 1967

### Molecular Orbital Symmetry Conservation in Transition Metal Catalyzed Transformations

Sir:

Woodward and Hoffmann have published a series of communications extending simple molecular orbital theory into the area of reaction chemistry.<sup>1</sup> This

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