results obtained by Birch, *et al.*,[45] from the incorporation of mevalonate-2-^{14}C into the terpenoid side chain of mycelianamide indicated that 80% of the radioactivity was not randomized, and it was suggested that the degree of randomization observed was more likely a result of the chemical degradative procedure than of a lack of specificity during biosynthesis. It is possible that the extent of randomization which can occur on the appropriate intermediate (*i.e.*, geranyl pyrophosphate) is subject to control at the enzyme level and by the pool size of the substrate. Insufficient knowledge exists on both of these points to permit a definite conclusion.

There may be several possible types of enzymatic control. For example, different enzyme inhibitors or different levels of enzyme may be present in the old and young plants. Also, it may be possible that the particular enzyme responsible for randomization of the monoterpenoid intermediate does not exist in the old plant. An analogous situation is known to occur in the rapid appearance and disappearance of diamine oxidase in pea seedlings.[46] Control by the substrate pool size can best be visualized by considering that the young plant has a rather large pool of monoterpenoid intermediate and that the two terminal methyls become equivalent. In the old plant perhaps only a small pool of monoterpenoid intermediate exists, and this substrate is immediately utilized in the biosynthesis and does not remain long for randomization of the methyl carbons to occur.

An alternative explanation, although remote, to the finding of randomization of label in the 1.3-year-old plant is the possibility of incorporation of mevalonate-U-^{14}C which has been formed by degradation of the administered mevalonate-2-^{14}C to $^{14}CO_2$ which, in turn, is reincorporated *via* CO_2 fixation. The results recently reported by Battu and Youngken[47] suggest that degradation of mevalonate to CO_2 and reincorporation of the latter into monoterpenes of *Mentha piperita* can occur.

Our data also support the mechanism of isomerization of isopentenyl pyrophosphate proposed first by Agranoff, *et al.*,[48] and later established by Shah, *et al.*[49] In this mechanism, the methylene carbon atom of isopentyl pyrophosphate is protonated, the proton from carbon atom 2 is discharged into the medium, and dimethylallyl pyrophosphate is formed. In the reverse reaction, a proton is added stereospecifically at carbon atom 2 of dimethylallyl pyrophosphate. Hence this isomerization does not result in a randomization of label originally present in the methylene group of isopentenyl pyrophosphate.

The metabolic relationship of mevalonate-2-^{14}C and β-skytanthine-^{14}C (Iβ) in 1.3-year-old plants and 3.0-year-old plants has been examined and this compound has been implicated in the biosynthesis of skytanthine by *Skytanthus acutus* M. The pathway for the biosynthesis of skytanthine isomers is not well understood. The contrast in our finding of randomization of label in β-skytanthine formed from mevalonate-2-^{14}C in 1.3-year-old plants with that of nonrandomization of label in 3.0-year-old plants requires additional study before its significance can be determined. Variation in an enzymatic reaction mechanism due to age appears to to be a new phenomenon.

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Communications to the Editor

Reactions of Vapor-Produced *t*-Butyl Carbonium Ion Injected into Liquid Isobutylene

Sir:

The reactions of specific, highly reactive hydrocarbon ions in the liquid phase are difficult to study directly. Ions may be produced in the liquid by direct liquid radiolysis, but the situation is complicated because many other reactive species such as electrons, radicals, and excited molecules are produced simultaneously. This complex situation may be simplified by producing specific ions in the vapor phase and injecting them by means of an electric field into a liquid or solid matrix. Under such conditions the positive ion is separated from its concomitant electron and is accelerated into the liquid or solid alone. To achieve this we describe a successful experimental method which is based on previous experiments by Schlag and Sparapany.[1,2] By this method we have studied the liquid phase reaction of *t*-butyl carbonium ion with isobutylene to form C_8 carbonium ions and their subsequent neutralization reactions.

The apparatus has been described.[3] A krypton resonance lamp[4,5] with intensity of greater than 10^{15} quanta/sec ionizes research grade isobutylene in the vapor phase. An electric field at right angles to the photon beam drives the positive ions into a detachable arm containing liquid isobutylene. The liquid arm of the cell extends into a dewar and is thermostated with a cold nitrogen gas stream; the temperature may be varied by changing the flow rate. A voltage of 400 v was applied to the external electrodes during photolysis. At $-128°$ the per cent conversion of isobutylene was linear beyond 120 min of photolysis time; the conversion rate was 0.01%/min. Gas chromatography showed

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that C_8 and C_{12} compounds comprised all detectable products; no products between C_8 and C_{12} were observed. Material balance calculations showed that the C_8 and C_{12} 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_8 or C_{12} products. These results support our contention that the positive ions are reacting in the *liquid* phase.

The C_8 products were analyzed on a $AgNO_3$–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_8 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_8 isomers reveal the probable structure of the C_8 carbonium ions and how they are neutralized.

Table I. Relative Yields of C_8 and C_{12} Products from t-$C_4H_9^+$ Reaction with Liquid Isobutylene[a]

Product	Yield, %
Relative Total Products	
C_8 products	73 ± 6
C_{12} products	27 ± 4
Relative C_8 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

[a] 120-min photolysis, −128°.

The krypton resonance lamp emits photons at 1236 A (10.0 ev) and 1165 A (10.6 ev) with relative intensities of 1.00 and 0.28, respectively.[6] The ionization potential of isobutylene is 9.4 ev, and the lowest appearance potential for a fragment ion from isobutylene is 11.3 ev ($C_4H_7^+$).[7] Therefore the only ion produced is the parent $C_4H_8^+$. Under our experimental pressure (0.05 torr) and nominal electric field (70 v/cm), we calculate that the $C_4H_8^+$ ion will make one or two collisions with isobutylene to form mainly t-$C_4H_9^+$ as shown by mass spectrometry[8–10] 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-$C_4H_9^+$ with some unreacted $C_4H_8^+$ also present.

t-$C_4H_9^+$ 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 neutralization reactions for the C_8 carbonium ions: one is hydride transfer to the carbonium ion to yield an alkane plus $C_4H_7^+$, and the other is proton transfer from the carbonium ion to give an alkene plus $C_4H_9^+$. 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 $C_4H_9^+$; it also demonstrates that we can obtain relative rates of ion–molecule reactions in certain liquids.

The other two C_8 products indicate somewhat surprisingly that t-$C_4H_9^+$ 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-$C_4H_9^+$ at both the primary and tertiary carbons in isobutylene is about 50%. Since t-$C_4H_9^+$ 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.

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Evidence for Trapped Dielectrons in Ice

Sir:

Electrons produced by γ radiation are trapped in hydroxide ices at 77°K. The trapped electron, e_t^-, is characterized by an epr singlet at $g = 2.001$,[1] a broad absorption band with a maximum at 5850 A,[2] and a hydroxide anion vacancy trapping site.[3] We have found that at high radiation doses e_t^- reacts to form a diamagnetic species which we believe to be best described as a dielectron, e_{2t}^{2-}, or two electrons trapped in the same hydroxide anion vacancy.

Frozen solutions of 10.0 and 6.0 *M* NaOH were γ irradiated at 77°K with Co^{60}. The yields of e_t^- and O^- 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_t^- 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_t^- yield above 8 Mrads; the optical absorption band shows a similar decrease. Since the O^- yield continues to increase over the entire dose range, and since no new para-

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