A New Method to Identify the Reaction Intermediates of Hydrogen Transfer or Exchange of Propene by Means of Microwave Spectroscopy

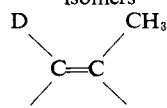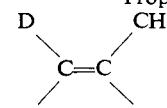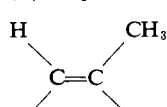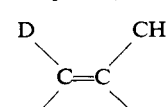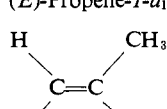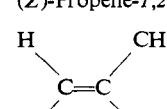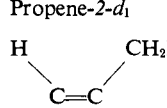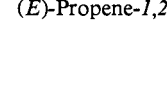Toshihiko Kondo,*[1a] Shuji Saito,[1a] and Kenzi Tamaru[1b]

Contribution from Sagami Chemical Research Center, Nishiohnuma, Sagamihara-shi, Kanagawa, 229, Japan, and the Department of Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113, Japan. Received April 22, 1974

Abstract: A method was proposed to identify the intermediates or the transition states of the hydrogen–deuterium exchange reaction of propene by means of microwave spectroscopic technique, determining the distribution of geometrical isomers of propene-d_1 and -d_2 formed during the course of the reaction. This method makes it feasible to identify many possible reaction intermediates: 1-propyl, 2-propyl, 1-propenyl, 2-propenyl, σ-allyl, and π-allyl intermediates as well as the transition state in the concerted mechanism. By the use of this method, the intermediate in the hydrogen exchange reaction of propene with deuteriosulfuric acid or deuteriophosphoric acid was demonstrated to be 2-propyl carbonium ion. The exchange reaction between propene and deuterium over $C_{24}K$ (potassium–graphite intercalation compound) was found to proceed through a π-allyl intermediate, and the exchange reaction between propene and deuterium oxide over bismuth molybdate (Bi:Mo = 1) was also demonstrated to take place *via* a σ-allyl intermediate.

Since microwave spectroscopy has extremely high resolution and high sensitivity, it can be applied to the reaction studies through the quantitative analyses of the gaseous molecules with permanent electric dipole moments. The rotational transition frequencies with which microwave spectroscopy concerns are dependent on the moments of inertia of the molecules and a slight difference in the moments of inertia gives a quite different spectrum.[2] Propene-d_1 has four geometrical isomers and propene-d_2 has seven isomers, as shown in Table I. The rotational transitions of these isomers are observed at the frequencies completely separated from each other. Hence, microwave spectroscopy can determine the amount of each of the geometrical isomers of propene-d_1 and -d_2, even in a mixture of all possible isomers (d_0, d_1, d_2, $\cdots$, d_6).[3] The quantitative analysis of these isomers is difficult with other methods. For example, mass spectrometry can determine the overall deuterium content of the propene molecules but cannot determine deuterium content at each hydrogen position of the propene.

Hirota and his coworkers[4] extensively studied the mechanisms of catalytic hydrogenations and exchange reactions of propene over various transition metals by means of microwave spectroscopic technique. The catalytic exchange reactions of propene by various transition metal complexes were also studied by others, using the microwave spectroscopic technique.[5–7] Sak-

Table I. The Geometrical Isomers of Propene-d_1 and Propene-d_2 (H = ^{1}H, D = ^{2}H, C = ^{12}C)

urai, *et al.*,[8] also investigated the *n*-butene isomerization over solid acids by the microwave spectroscopic quantitative analysis of 1- and (Z)-2-butene-d_1 species. Some of the above results were not enough to identify the reaction intermediates since variation of the distributions of propene-d_1 and -d_2 isomers during the course of the reaction was not studied.

We propose a new method to identify reaction intermediates, following the change of the distributions not only of propene-d_1 but also of propene-d_2 isomers during

(1) (a) Sagami Chemical Research Center; (b) The University of Tokyo.

(2) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1955.

(3) (a) Y. Morino and E. Hirota, *J. Chem. Soc. Jap., Pure Chem. Sect.,* **85**, 535 (1964); E. Hirota, *Shokubai*, **13**, 31 (1971); (b) L. H. Scharpen, R. F. Rauskolb, and C. A. Tolman, *Anal. Chem.*, **44**, 2010 (1972).

(4) K. Hirota, Y. Hironaka, and E. Hirota, *Tetrahedron Lett.*, 1645 (1964); T. Ueda, J. Hara, K. Hirota, S. Teratani, and N. Yoshida, *Z. Phys. Chem. (Frankfurt am Main)*, **64**, 64 (1969); K. Hirota and Y. Hironaka, *Bull. Chem. Soc. Jap.*, **39**, 2638 (1966); K. Hirota and Y. Hironaka, *J. Catal.*, **4**, 602 (1965).

(5) K. Hirabayashi, S. Saito, and I. Yasumori, *J. Chem. Soc., Faraday Trans. 1*, **68**, 978 (1972).

(6) T. Ueda, *Int. Congr. Catal., 5th* (1972); in "Catalysis," Vol. 1, J. W. Hightower, Ed., North-Holland, Amsterdam, 1973, R431.
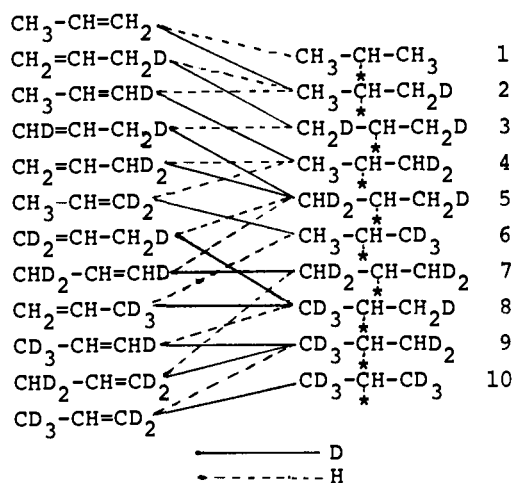
(7) C. A. Tolman and L. H. Scharpen, *J. Chem. Soc., Dalton Trans.*, 584 (1973).

(8) Y. Sakurai, Y. Kaneda, S. Kondo, E. Hirota, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, **67**, 3275 (1971).

Figure 1. Reaction scheme of all the deuteriopropene formation through the 2-propyl intermediate.

Figure 2. Graph of the 2-propyl intermediate mechanism: ●, deuteriopropenes; ○, 2-propyl intermediates.

the course of the hydrogen–deuterium exchange reaction of propene by means of microwave spectroscopy. The application of this method to a few examples will be demonstrated in the present paper.

Theory

Reaction Intermediates. For the hydrogen exchange between propene and a substance containing deuterium, at least one of the hydrogen atoms of the propene molecule should be dissociated prior to, after, or simultaneously with the deuterium atom addition to propene, dissociative, associative, or concerted mechanism,[9] respectively. In the associative mechanism, there are two intermediates, namely, 1-propyl and 2-propyl ones, the half-hydrogenated state of olefin in heterogeneous catalysis.[10] In the dissociative mechanism, there are many possible intermediates: 1-propenyl,[11] 2-propenyl,[11] σ-allyl,[12] and π-allyl[13] ones.

It is usually accepted that the exchange reactions through these intermediates proceed consecutively by single exchange steps. If the reaction proceeds by multiple exchange processes, or if the rate of the adsorption–desorption process of propene is slower than that of the exchange process, the propene containing more than one deuterium atom is produced even at the initial stage of the reaction. In our experiments, mass spectrometric measurement of the deuteriopropene formed has demonstrated no such multiple exchange but the stepwise exchange reaction.

Let us consider the distributions of propene-d_1 and -d_2 isomers formed during the course of the reactions via these possible intermediates.

Distributions of Propene-d_1 and -d_2 Isomers. (a) 1-Propyl Intermediate.

$$CH_2{=}CHCH_3 \xrightarrow{+D} \underset{*}{CH_2CHDCH_3} \xrightarrow{-H} CH_2{=}CDCH_3 \quad (1)^{14}$$

From the 1-propyl intermediate, only propene-2-d_1 should appear as shown in (1). When the added deuterium is a deuteron, the intermediate is the 1-propyl carbonium ion, which may rearrange to protonated cyclopropane.[15] In this case, propene-1-d_1 and propene-3-d_1 may be produced by intramolecular hydride shift and/or carbon migration of protonated cyclopropane.

(b) 2-Propyl Intermediate.

$$CH_2{=}CHCH_3 \xrightarrow{+D} \underset{*}{CH_2DCHCH_3} \xrightarrow{-H}$$

$$\begin{cases} CHD{=}CHCH_3 & 40\% \\ CH_2DCH{=}CH_2 & 60\% \end{cases} \quad (2)$$

$$CHD{=}CHCH_3 \xrightarrow{+D} \underset{*}{CHD_2CHCH_3} \xrightarrow{-H}$$

$$\begin{cases} CD_2{=}CHCH_3 & 10\% \\ CHD_2CH{=}CH_2 & 30\% \end{cases} \quad (3)$$

$$CH_2DCH{=}CH_2 \xrightarrow{+D} \underset{*}{CH_2DCHCH_2D} \xrightarrow{-H}$$

$$CHD{=}CHCH_2D \quad 60\%$$

The 2-propyl intermediate, $CH_2DC^*HCH_3$, formed by the addition of a deuterium atom to propene, will produce propene-d_1 isomers by dissociating one of the five hydrogen atoms of the two methyl groups, as shown in the reaction 2. The composition of the d_1 species formed should be propene-3-d_1 60% and propene-1-d_1 40%, according to an equal probability of the dissociation of each hydrogen atom of CH_2D and CH_3, if the secondary kinetic isotope effect is neglected. Under similar consideration, the distribution of propene-d_2 isomers should be propene-1,1-d_2 10%, propene-1,3-d_2 60%, and propene-3,3-d_2 30% as shown in reaction 3. These initial distributions of propene-d_1 and -d_2 isomers are the same as those in the equilibrium distribution, since the five hydrogen atoms of methyl and methylene groups of propene equally take part in the exchange reaction (see Figures 1 and 2). Therefore, it is important to note that in the 2-propyl intermediate mechanism the distributions of propene-d_1 and -d_2 isomers remain constant throughout the course of the reaction.

The reaction scheme of all the deuteriopropene production through the 2-propyl intermediate is shown in Figure 1, where the solid and dotted lines represent the reversible processes in which deuterium and hydrogen participate, respectively. In order to illustrate the topological property in the reaction scheme, a graph is

(9) (a) J. Turkevich and R. K. Smith, *J. Chem. Phys.*, **16**, 466 (1948); (b) C. G. Swain and J. F. Brown, Jr., *J. Amer. Chem. Soc.*, **74**, 2538 (1952); (c) D. M. Brouwer, *J. Catal.*, **1**, 22 (1962).

(10) J. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

(11) R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).

(12) J. Powell, S. D. Robinson, and B. L. Shaw, *Chem. Commun.*, **78** (1965).

(13) (a) W. M. H. Sachtler, *Recl. Trav. Chim. Pays-Bas*, **82**, 243 (1963); (b) C. R. Adams and T. J. Jennings, *J. Catal.*, **2**, 63 (1963).

(14) The asterisk (*) represents cation (+), radical (·), anion (−) σ-bond between metal atom (ion) and carbon or adsorption (coordina-
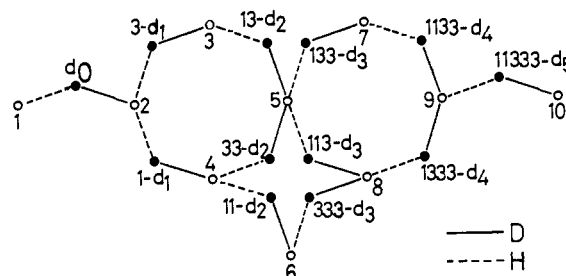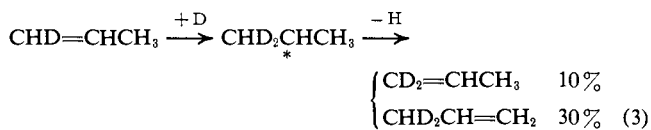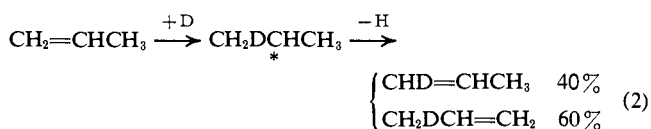
tion) site. In the present consideration, the discussion about the electronic states of the intermediates is not necessary.

(15) C. J. Collins, *Chem. Rev.*, **69**, 543 (1969).

given in Figure 2 where solid and blank circles represent deuteriopropenes and the intermediates, respectively. The numberings of the blank circles in Figure 2 correspond to those of the intermediates in Figure 1. The important point in understanding Figure 2 is that propene-1-d_1 and propene-3-d_1 are simultaneously formed through the intermediate 2 and that propene-$1,3$-d_2, and propene-$3,3$-d_2 and propene-$1,1$-d_2 are simultaneously produced through the intermediates 3 and 4, respectively, as the second products. This is quite different from the π-allyl intermediate mechanism and the concerted mechanism to be described below.

(c) 1-Propenyl Intermediate. This intermediate contains (Z)-1-propenyl and (E)-1-propenyl intermediates.

$$(4)$$

$$(5)$$
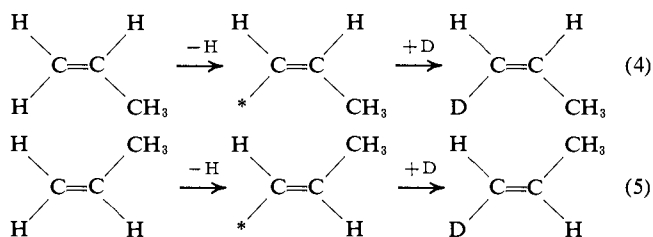
According to reactions 4 and 5, (Z)-propene-1-d_1 and (E)-propene-1-d_1 are formed through (Z)-1-propenyl and (E)-1-propenyl intermediates, respectively.

(d) 2-Propenyl Intermediate.

$$(6)$$
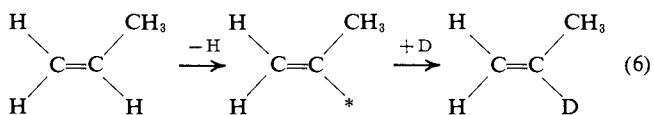
Propene-2-d_1 is the only product through the 2-propenyl intermediate. This distribution of propene-d_1 isomers is the same as that of the 1-propyl intermediate mechanism. However, no cis–trans isomerization of olefin takes place through the 2-propenyl intermediate as shown in reaction 6. On the other hand, the isomerization necessarily occurs with the exchange reaction through the 1-propyl intermediate as shown in reaction 7. Accordingly, if (Z)-propene-1-d_1 instead of pro-

$$(7)^{16}$$
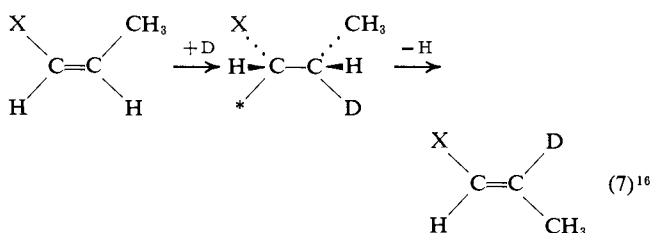
pene-d_0 is the reactant $(X = D)$, (Z)-propene-$1,2$-d_2 should be obtained through the 2-propenyl intermediate and (E)-propene-$1,2$-d_2 should be produced in the 1-propyl intermediate mechanism as shown in reaction 7.[16]

(e) σ-Allyl Intermediate.

$$CH_2=CHCH_3 \xrightarrow{-H} CH_2=CHCH_2 \xrightarrow{+D} CH_2=CHCH_2D \quad (8a)$$

$$CH_2=CHCH_2D \xrightarrow{-H} CH_2=CHCHD \xrightarrow{+D} CH_2=CHCHD_2 \quad (8b)$$

(16) In reaction 7, it is assumed that both deuterium addition and hydrogen elimination occur on the same side of the olefin as that for the adsorption site, which results in the cis addition–elimination.
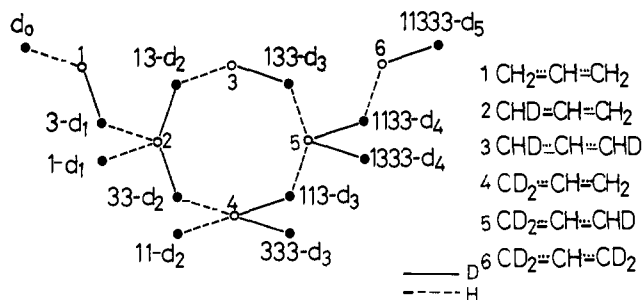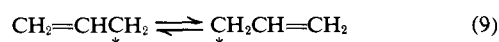
Figure 3. Graph of the π-allyl intermediate mechanism: ●, deuteriopropenes; ○, π-allyl intermediates.

According to reaction 8, propene-3-d_1 and propene-$3,3$-d_2 are only formed through the σ-allyl intermediate as mono- and dideuteriopropenes, respectively. No deuteriopropene containing more than three deuterium atoms should appear from this mechanism.

If reaction 9 is extremely faster than the exchange process, the distributions of propene-d_1 and -d_2 isomers should be the same as those for the π-allyl intermediate mechanism.[17a] In this case, the intermediate may be called the dynamic σ-allyl intermediate.[12]

$$CH_2=CHCH_2 \rightleftharpoons CH_2CH=CH_2 \quad (9)$$

(f) π-Allyl Intermediate. The reaction scheme for the π-allyl intermediate mechanism is given in Figure 3. The π-allyl intermediate 1 is formed by dissociating one of the three hydrogen atoms of the methyl group of propene, and its both end carbons, C-1 and C-3, become equivalent. Propene-d_1 isomers are formed by adding a deuterium atom (adsorbed) to one of the two methylene groups of π-allyl intermediate 1. Consequently, the propene-d_1 isomer initially produced is only propene-3-d_1. However, propene-1-d_1, propene-$1,3$-d_2, and propene-$3,3$-d_2 are subsequently produced by repeating the mechanism; propene-$1,3$-d_2 and propene-$3,3$-d_2 are equally produced by the deuterium atom addition to the intermediate 2. Propene-$1,1$-d_2 will also be produced through the intermediate 4. According to this mechanism, since propene has five hydrogen atoms which participate in the exchange reaction, the statistical distribution of propene-d_1 and -d_2 isomers in the exchange equilibrium is the same as that for the 2-propyl intermediate mechanism. However, it is a strong contrast that the distributions of propene-d_1 and -d_2 isomers in the π-allyl intermediate mechanism vary during the course of the reaction.

(g) Concerted Mechanism. In this mechanism, which has been familiar as a bifunctional catalysis,[9] one of the hydrogen atoms of the methyl group of propene is dissociated, a deuterium atom being simultaneously

(17) (a) The following scheme indicates that propene-1-d_1 and propene-$1,3$-d_2 are formed through dynamic σ-allyl intermediate.
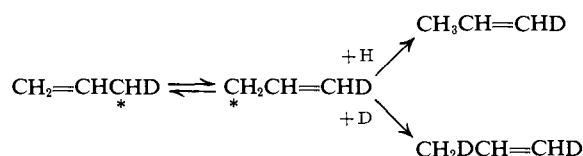
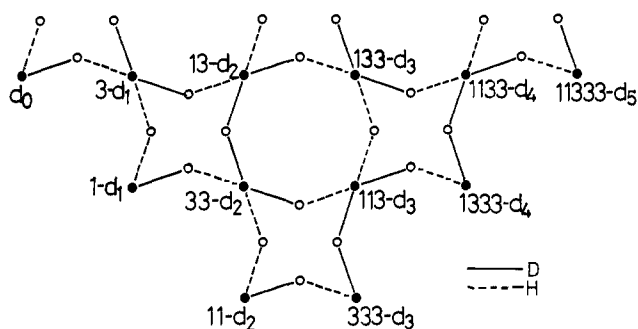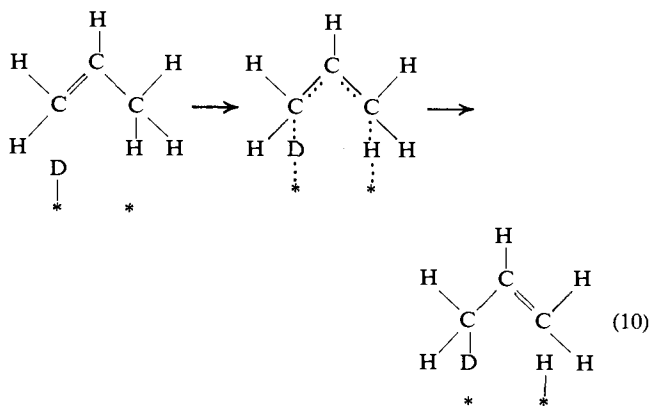(b) For a recent review, see D. H. Rouvray, Chem. Brit., 10, 11 (1974).

Figure 4. Graph of the concerted mechanism: ●, deuteriopropenes; ○, transition states of the concerted mechanism.

added to the methylene group of the propene as shown in reaction 10. The initial product is, accordingly, only

(10)

propene-3-d_1. The graph of the concerted mechanism is illustrated in Figure 4. Propene-1-d_1 and propene-1,3-d_2 are subsequently produced by repeating similar processes as demonstrated in the figure. The third products are propene-3,3-d_2 and propene-1,3,3-d_3. Propene-1,1-d_2 is one of the fourth products as demonstrated by the graph.

The topological graphs[17b] shown in Figures 2, 3, and 4 reveal the correlations among various deuteriopropene isomers. All the graphs indicate bilateral symmetries between the d_0–d_2 and d_3–d_5 regions, which justifies the procedure to elucidate the mechanism of the whole isotopic exchange by examining the distributions of only the d_1 and d_2 species. The change of the compositions of these isomers for each of the mechanisms is schematically summarized in Figure 5, which demonstrates the different distributions of propene-d_1 and -d_2 isomers with the reaction time for possible reaction mechanism. From Figures 5f and 5g, it is clear that the distributions of propene-d_1 isomers are the same both in π-allyl intermediate mechanism and in the concerted mechanism, but the distributions of propene-d_2 isomers can clearly tell the difference between the π-allyl intermediate mechanism and the concerted mechanism.

Results and Discussion

Examples of 2-Propyl Intermediate. The distributions of propene-d_1 and -d_2 isomers formed during the course of the hydrogen–deuterium exchange reaction between propene and deuteriophosphoric acid (D_3PO_4) at 28° are shown in Table II. The overall deuterium contents of propene are also given in Table II, which
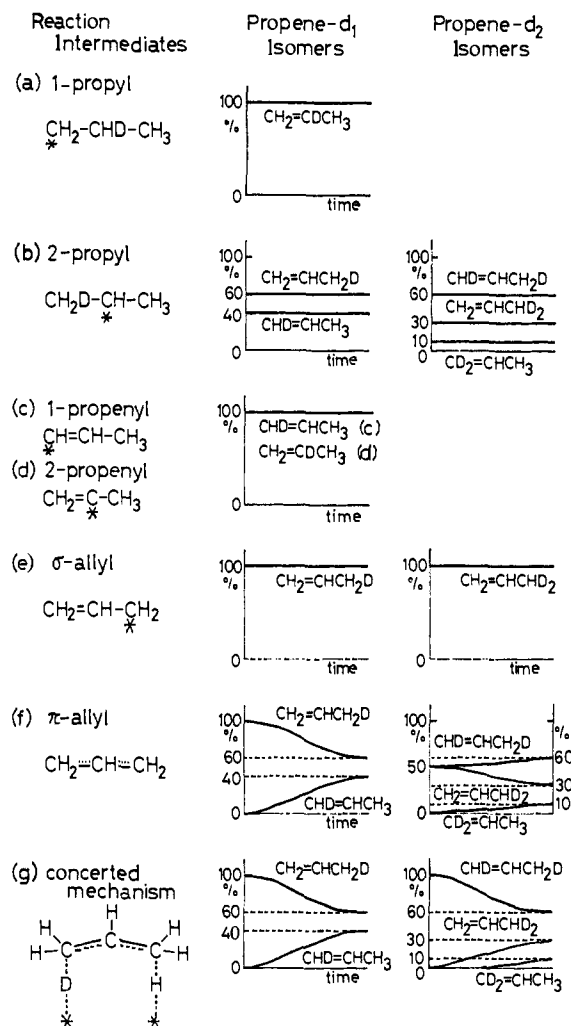

Figure 5. Distributions of propene-d_1 and -d_2 isomers formed through the various reaction intermediates.

Table II. Distributions of Propene-d_1 and -d_2 Isomers (%) Formed during the Hydrogen Exchange Reaction between Propene and D_3PO_4 at 28°

	Reaction time, hr					
	20	68.5	76	118	144	170
(Z)-Propene-1-d_1	19.5	18.7	19.2	17.5	18.0	18.4
(E)-Propene-1-d_1	27.4	21.7	21.2	20.5	20.0	19.6
Propene-3-d_1	53.1	59.6	59.6	62.0	62.0	62.0
Propene-2-d_1	0	0	0	0	0	0
Propene-1,1-d_2				10.7	10.6	10.13
(Z)-Propene-1,3-d_2				24.0	24.1	23.6
(E)-Propene-1,3-d_2				29.7	28.8	30.0
Propene-3,3-d_2				35.6	36.5	36.
Propene-2,3-d_2, etc.				0	0	0
Propene-d_0 (%)[a]	98.5	88.5	86.5	69.9	52.3	37.2
Propene-d_1	1.5	8.9	10.8	23.0	34.1	42.0
Propene-d_2	0	2.6	2.2	6.1	11.1	16.9
Propene-d_3	0	0	0.4	0.9	2.2	3.5

[a] All mass spectra have been corrected for abundance of ^{13}C.

were obtained by mass spectrometry, using an ionization voltage of ca. 10 V to avoid fragmentation. The results indicate that the reaction did not proceed through multiple exchange processes but through successive single exchange steps. Since no propene-2-d_1 is produced throughout the reaction, neither the 1-propyl carbonium ion nor protonated cyclopropane[15] should
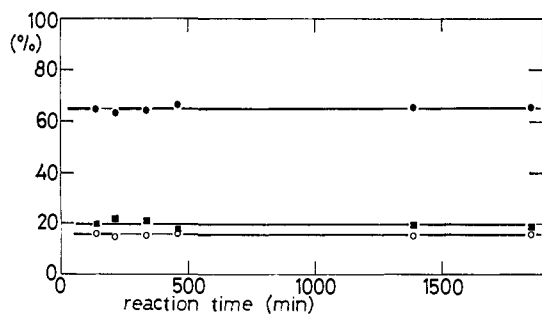
Figure 6. Distributions of propene-d_1 isomers formed during the hydrogen exchange reaction between propene and D_2SO_4 at 28°: ●, propene-3-d_1; ○, (Z)-propene-1-d_1; ■, (E)-propene-1-d_1.
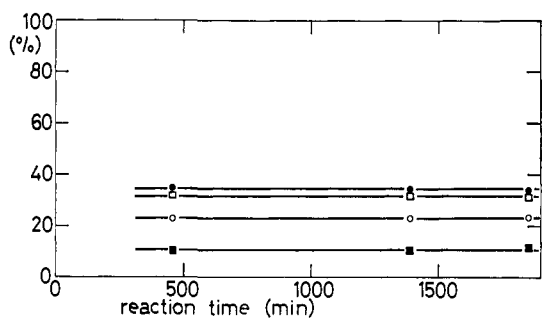

Figure 7. Distributions of propene-d_2 isomers formed during the hydrogen exchange reaction between propene and D_2SO_4 at 28°: ●, propene-$3,3$-d_2; ○, (Z)-propene-$1,3$-d_2; □, (E)-propene-1-3-d_2; ■, propene-$1,1$-d_2.

Figure 8. Deuterium contents of propene during the hydrogen exchange reaction between propene and deuterium over $C_{24}K$ at 120°: ○, propene-d_0; ×, propene-d_1; □, propene-d_2; ●, propene-d_3.

Figure 9. Distributions of propene-d_1 isomers formed during the hydrogen exchange reaction between propene and deuterium over $C_{24}K$ at 120°. Mean deuterium content Ψ is represented by the equation $\Psi = 100(\Sigma_{i=1}^{6} i d_i / 6\Sigma_{j=0}^{6} d_j)$: ●, propene-$3$-$d_1$; ×, ($Z$)-propene-$1$-$d_1$; ○, ($E$)-propene-$1$-$d_1$.

be the intermediate of this exchange reaction. Table II also shows that the concerted mechanism and π-allyl intermediate mechanism are excluded and that the distributions of propene-d_1 and -d_2 isomers are in good agreement with those of the 2-propyl intermediate mechanism. Therefore, it is concluded that this reaction proceeds through the formation of 2-propyl carbonium ion. The results for deuteriosulfuric acid (D_2SO_4) are shown in Figures 6 and 7. Due to similar consideration as described above, these results also exhibit that the reaction intermediate is the 2-propyl carbonium ion. Consequently, our results deny the concerted mechanism proposed by Turkevich and Smith.[9a,18] It is also shown that neither sulfuric acid nor phosphoric acid should be a bifunctional catalyst[9b] and also that they are not tautomeric catalysts[20] in this reaction.

The concepts of bifunctional catalyst and tautomeric catalyst have been proposed for acid–base catalysis on the basis of the anomalously high catalytic activities and the molecular structures of these catalysts. However, the results we have obtained supplied no evidence in support of these concepts. The hydrogen exchange reaction between propene and deuterated p-toluene-sulfonic acid supported on silica gel was investigated by

use of the microwave technique and the reaction proceeded through the 2-propyl carbonium ion even in a heterogeneous system.[21]

Examples of π-Allyl Intermediate.[22] The hydrogen exchange reaction of propene with deuterium was studied over the potassium graphite intercalation compound $C_{24}K$. When a mixture of propene and D_2 was introduced onto the catalyst at 120°, simultaneous hydrogenation and hydrogen exchange reaction of the propene took place. The amounts of the various deuteriopropenes were determined by mass spectrometry, as shown in Figure 8. It is shown that the hydrogen exchange reaction did not proceed through multiple exchange processes but through successive single exchange steps. The results of microwave spectroscopic measurements of propene-d_1 isomers are shown in Figure 9 and those of propene-d_2 isomers in Table III. Figure 9 shows a good agreement with

Table III. Distributions of Propene-d_2 Isomers (%) during the Exchange Reaction between Propene and D_2 over $C_{24}K$ at 120°

$\Psi,^a$ %	6.6	9.6	34.6
Propene-$1,1$-d_2	3	6	8
(Z)-Propene-$1,3$-d_2	22	22	26
(E)-Propene-$1,3$-d_2	25	28	31
Propene-$3,3$-d_2	50	44	35
Propene-$2,3$-d_2, etc.	0	0	0

^{a} Mean deuterium content is represented by the equation $\Psi = 100(\Sigma_{i=1}^{6} i d_i / 6\Sigma_{j=0}^{6} d_j)$.

(18) Turkevich and Smith examined the hydrogen–tritium exchange reactions of ethylene and propene with tritiated phosphoric acid and obtained the results that the reaction proceeds in the case of propene but not in the case of ethylene. They considered these results as evidence for concerted mechanism. However, these results can be understood on the base of the carbonium ion intermediate mechanism since ethyl carbonium ion requires a higher energy of formation (ca. 27 kcal/mol)[19] than 2-propyl carbonium ion.

(19) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

(20) P. R. Rony, *J. Amer. Chem. Soc.*, **90**, 2824 (1968); **91**, 6090 (1969).
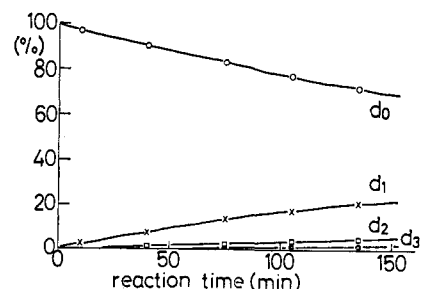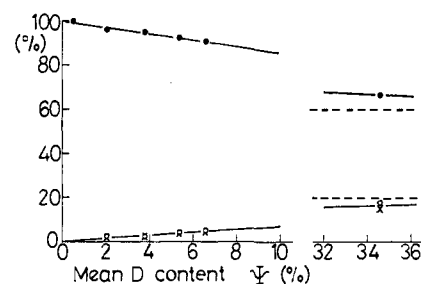
(21) T. Kondo, M. Ichikawa, S. Saito, and K. Tamaru, *J. Phys. Chem.*, **77**, 299 (1973).

(22) As a preliminary report, see T. Kondo, M. Ichikawa, S. Saito, and K. Tamaru, *Bull. Chem. Soc. Jap.*, **45**, 1580 (1972).

the distributions of propene-d_1 isomers in Figures 5f and 5g. This suggests that the reaction has either a π-allyl intermediate mechanism or a concerted mechanism. The distributions of propene-d_2 isomers in Table III are similar to those of propene-d_2 isomers in Figure 5f. Therefore, the intermediate of this exchange reaction is π-allyl. By means of the microwave spectroscopic technique, it was also demonstrated that the hydrogen exchange reaction between propene and deuterium over zinc oxide proceeds through the π-allyl intermediate.[23]

Example of σ-Allyl Intermediate. The propene gas saturated with deuterium oxide vapor was allowed to pass over bismuth molybdate (Bi:Mo = 1) catalyst at 100° in a closed circulation system. The results of the microwave and the mass analyses are shown in Table IV.
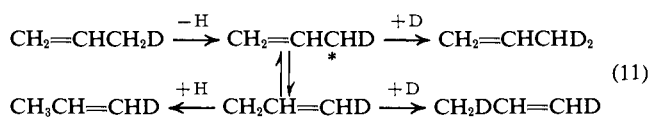
Table IV. Distributions of Propene-d_1 and -d_2 Isomers (%) Formed during the Hydrogen Exchange Reaction between Propene and D_2O over Bismuth Molybdate (Bi:Mo = 1) at 100°

| | Reaction time | | | | | |
	250 min	645 min	1910 min	3 days	6 days	23 days
(Z)-Propene-1-d_1	0	0	0.5	0.6	1.2	2.1
(E)-Propene-1-d_1	0	0	0.6	0.9	1.7	2.1
Propene-3-d_1	100	100	98.9	98.5	97.1	95.8
Propene-2-d_1	0	0	0	0	0	0
Propene-$1,1$-d_2			0	0.5	0.8	1.1
(Z)-Propene-$1,3$-d_2			0	2.0	2.7	3.2
(E)-Propene-$1,3$-d_2			0	3.0	2.9	3.4
Propene-$3,3$-d_2			100	94.5	93.6	92.3
Propene-$2,3$-d_2, etc.			0	0	0	0
Propene-d_0 (%)[a]	92.9	84.3	69.4	47.9	36.1	15.5
Propene-d_1	7.1	14.7	26.6	39.3	42.9	39.3
Propene-d_2	0	1.0	3.6	10.6	18.4	33.8
Propene-d_3	0	0	0.2	2.2	2.6	10.8

[a] All mass spectra have been corrected for abundance of ^{13}C.

The main parts of propene-d_1 and -d_2 isomers are propene-3-d_1 and propene-$3,3$-d_2, respectively, throughout the course of the reaction. Consequently, this reaction proceeds through the σ-allyl intermediate since the hydrogen atoms of the methyl group of propene are predominantly exchangeable (see Figure 5e).

The results of the exchange reaction at 300° are given in Table V. The distributions of propene-d_1 isomers are similar to those in Figures 5f and 5g, but the initial distribution of propene-d_2 isomers (propene-$1,3$-d_2 30%, propene-$3,3$-d_2 70%) is in disagreement with any mechanisms in Figure 5. The concerted mechanism should be excluded because the initial distribution of propene-d_2 isomers in the concerted mechanism contains no propene-$3,3$-d_2. The initial distribution of propene-d_2 isomers in Table V is between those of σ-allyl and π-allyl intermediates. When the double bond of the σ-allyl intermediate spontaneously migrates as shown in process 9, propene-1-d_1 and propene-$1,3$-d_2 should be formed since reaction 8b is changed to reaction 11.

$$CH_2{=}CHCH_2D \xrightarrow{-H} CH_2{=}CHCHD \xrightarrow{+D} CH_2{=}CHCHD_2$$

$$CH_3CH{=}CHD \xleftarrow{+H} CH_2CH{=}CHD^* \xrightarrow{+D} CH_2DCH{=}CHD \quad (11)$$

Table V. Distributions of Propene-d_1 and -d_2 Isomers (%) Formed during the Hydrogen Exchange Reaction between Propene and D_2O over Bismuth Molybdate (Bi:Mo = 1) at 300°

| | Reaction time | | | | | |
	10 min	25 min	45 min	185 min	1872 min	9 days
(Z)-Propene-1-d_1	3.6	3.7	4.8	7.2	10.4	13.7
(E)-Propene-1-d_1	4.8	4.6	4.9	6.8	10.3	15.4
Propene-3-d_1	91.6	91.7	90.3	86.0	79.3	70.9
Propene-2-d_1	0	0	0	0	0	0
Propene-$1,1$-d_2				0	5.1	6.6
(Z)-Propene-$1,3$-d_2				13.4	23.0	24.3
(E)-Propene-$1,3$-d_2				17.1	25.0	26.4
Propene-$3,3$-d_2				69.5	46.9	42.7
Propene-$2,3$-d_2, etc.				0	0	0
Propene-d_0 (%)[a]	97.8	94.9	93.4	87.6	81.7	70.3
Propene-d_1	2.2	4.9	6.4	10.9	16.5	24.4
Propene-d_2	0	0.2	0.2	1.3	1.5	4.4
Propene-d_3		0	0	0.2	0.3	0.8

[a] All mass spectra have been corrected for abundance of ^{13}C.

The more rapid reaction 9 becomes, the more the distributions of propene-d_1 and -d_2 isomers of the σ-allyl intermediate mechanism are consistent with those of the π-allyl intermediate mechanism, as described in Theory (section e). Therefore, Table V demonstrates that the intermediate of this reaction is a dynamic σ-allyl species. From our results, it was concluded that the σ-allyl intermediate is formed on bismuth molybdate at lower temperatures in the hydrogen exchange reaction between propene and deuterium oxide, and that at higher temperatures the intermediate becomes dynamic since reaction 9 takes place.

As an example of a dynamic species, it has been known that the proton nuclear magnetic resonance spectrum of allylmagnesium bromide C_3H_5MgBr in ether demonstrates the allyl ligand to be a dynamic σ-allyl species.[24] The diallylzinc $(C_3H_5)_2Zn$ gives a typical pmr spectrum of a dynamic σ-allyl system at 20° in tetrahydrofuran and at $-100°$ another peculiarity, namely, the conversion of the dynamic σ-allyl into the static σ-allyl system.[25] On the other hand, it was found that the surface of the catalyst remained in the initial state at 100° but was gradually reduced at 300° by propene.

It has generally been accepted that bismuth molybdate is a selective catalyst for the oxidation of propene to acrolein. There are many investigations on the mechanism of this reaction,[13,26] whereby the rate-determining step has been known to be the abstraction of the α hydrogen of propene to form a symmetric allylic intermediate, through which the oxidation reaction proceeds to produce acrolein. These results are acceptable not only for the π-allyl intermediate mechanism but also for the dynamic σ-allyl intermediate mechanism.

The reaction intermediates in other catalytic systems were also studied. It was reported that the deuterium–propene exchange reactions proceed through 1-propyl and 1-propenyl intermediates over nickel phthalocya-

(23) S. Naito, T. Kondo, M. Ichikawa, and K. Tamaru, *J. Phys. Chem.*, **76**, 2184 (1972).

(24) J. E. Nordland and J. D. Roberts, *J. Amer. Chem. Soc.*, **81**, 1769 (1959).

(25) G. Wilke, B. Bogdanović, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmermann, *Angew. Chem., Int. Ed. Engl.*, **5**, 151 (1966).

(26) C. C. McCain, G. Gough, and G. W. Godin, *Nature (London)*, **198**, 989 (1963).

nine–alkali metal EDA complexes,[27] and over activated alumina,[28] respectively.

By use of our method, the reaction intermediate of a given system for the consecutive hydrogen–deuterium exchange reactions of propene can be identified without any direct observation of the adsorbed (coordinated) state of propene, because the propene-d_1 and -d_2 isomers are formed according to the behavior of the reaction intermediate.

Experimental Section

The deuteriosulfuric acid was prepared from 3 ml of concentrated H_2SO_4 and 10 ml of D_2O (99.7%; Merck Co.). Water of the solution was distilled *in vacuo* and the concentration of sulfuric acid was about 80%. The initial pressure of propene fed was about 300 Torr. The reaction was carried out at 28° in an ampoule (*ca.* 270 ml) with a magnetic stirrer.

The 5 ml of deuteriophosphoric acid (deuterium content 99%, density 1.75 g/cm³) of Merck Co. was used without further purification. The initial pressure of propene fed was about 250 Torr. The reaction was carried out at 28° in an ampoule (*ca.* 270 ml) with a magnetic stirrer.

The deep blue $C_{24}K$ (potassium graphite intercalation compound) was prepared by heating 2.0 g of spectroscopic powder graphite (Union Carbide Co.) with *ca.* 0.5 g of distilled potassium metal *in vacuo* at 380° for 24 hr. A conventional closed circulating system (*ca.* 350 ml) was used to study the exchange reaction. The catalyst was exposed to deuterium gas D_2 (200 Torr) at 120° for 15 hr and was then evacuated for about 10 min.

The bismuth molybdate was precipitated from an ammonium molybdate solution by addition of bismuth nitrate solution and aqueous ammonia to give a bismuth to molybdenum ratio of 1:1. The catalyst was thoroughly washed with water, dried, then calcined at 550° in air. The propene gas (150–200 Torr) saturated with deuterium oxide vapor (deuterium content 99%) was allowed to pass over bismuth molybdate (5.3 g) in a closed circulation system (*ca.* 350 ml). The mole ratio of the propene to deuterium oxide fed was 1:5.

The quantitative analysis of the geometrical isomers of propene-d_1 and propene-d_2 was carried out by using the conventional microwave spectrometer with 110-kHz sinusoidal Stark modulation.[29] A pair of ferrite isolators were put in front of and behind the absorption cell so as to prevent multiple reflection of the microwave in the absorption cell.[3a,30] A precise step attenuator for the detection and amplification circuit was not used in this study because detector nonlinearities were found to be within 0.1% when the intensities of the absorption lines compared were not strong and their ratio was between 0.01 and 100.[31] The absorption cell of a 3-m waveguide was maintained at Dry Ice temperature.

The $1_{01} \leftarrow 0_{00}$ rotational transitions were used in the measurements; their frequencies for various isomers are listed in Table VI. For accurate measurements of intensity ratios, it is essential that the two lines compared are located as closely as possible. D_3 species and D_4 species are chemically equivalent; the relative abundance of D_3 species to D_4 species is $^1/_2$. Therefore, the pairs of D_2 and D_4, D_1 and D_3, and D_6 and D_3 species were used in the quantitative analysis of propene-d_1 isomers. For example, the absorption line of D_2 species was recorded three times and then that of D_4 species was immediately recorded three times. This procedure was repeated two or three times. The intensity ratio of $D_2:D_4$ was calculated from the average values of these observed intensities.

In the analysis of propene-d_2 isomers, six pairs were used under the same principle, as listed in Table VII. The sample pressure was 20 mTorr and the current in the crystal detector was 100 μA. No change in sample pressure and composition was observed during the measurements.

The maximum absorption coefficient[2] for a rotational transition of the asymmetric top molecule is

$$\gamma_{max} = \frac{8\pi h N f_v}{3c(kT)^2} \sqrt{\frac{\pi h ABC}{kT}} \exp(-E_r/kT)(2J+1)|\mu_{ij}|^2 \frac{\nu_0^2}{\Delta\nu}$$

(27) S. Naito, M. Ichikawa, S. Saito, and K. Tamaru, *J. Chem. Soc., Faraday Trans. 1*, **69**, 685 (1973).

(28) Y. Sakurai, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, **67**, 3094 (1971); *Bull. Chem. Soc. Jap.*, **45**, 980 (1972).

(29) S. Saito, *J. Mol. Spectrosc.*, **30**, 1 (1969).

Table VI. Frequencies of the $1_{01} \leftarrow 0_{00}$ Rotational Transitions of Propene-d_1 and Propene-d_2 Isomers[a]

Species[b]	Freq, MHz	Species[b]	Freq, MHz
D_6	17139.00	D_4D_6	16104.01
D_3	16832.95	D_3D_4	15864.90
D_1	16769.76	D_2D_6	15835.80
D_4	16377.12	D_1D_4	15751.82
D_2	16090.18	D_1D_2	15550.79
D_3D_6	16542.01	D_2D_3	15534.33
D_1D_6	16489.77	D_4D_5	15482.30
D_1D_3	16218.95	D_2D_4	15140.28

[a] E. Hirota, *Shokubai*, **13**, 31 (1971). [b] The numbering of D denotes the position of the deuterium atom substituted for a hydrogen atom. The numbering of hydrogen positions is as follows
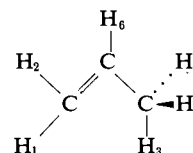
H_3, H_4, and H_5 are chemically equivalent, but H_3 can be spectroscopically distinguished from H_4 and H_5 which are equivalent in both senses.

Table VII. Correction Coefficients for the Intensity of Ratios between Propene-d_1 Isomers and between Propene-d_2 Isomers

Ratios	f_v	$(ABC)^{1/2}$	μ_a^2	ν_0^2	Total corrections
$D_2:D_4$	1.0740	1.0117	0.9961	0.9653	1.0448
$D_1:D_3$	1.0740	0.9922	1.0196	0.9925	1.0783
$D_6:D_3$	1.0740	0.9871	1.0090	1.0367	1.1089
$D_1D_4:D_3D_4$	1.0625	0.9926	1.0196	0.9858	1.0600
$D_1D_2:D_2D_3$	1.0740	0.9942	1.0197	1.0021	1.0911
$D_2D_3:D_4D_5$	1.0625	1.0098	0.9851	1.0067	1.0640
$D_4D_6:D_3D_4$	1.0625	0.9871	1.0090	1.0304	1.0904
$D_2D_6:D_3D_4$	1.1411	0.9939	1.0050	0.9963	1.1355
$D_1D_6:D_3D_6$	1.0740	0.9918	1.0197	0.9937	1.0793

where N is the number of molecules per cubic centimeter, f_v is the fraction of molecules in the occupied vibrational state, A, B, and C are the rotational constants, E_r is the rotational energy of the lower state, J is the total angular momentum quantum number, μ_{ij} is the dipole moment matrix element for the transition, ν_0 is the transition frequency, $\Delta\nu$ is the half-width of the line at half-maximum intensity, and other notations have their usual significances. As some of these parameters have slightly different values in isotopic isomers, it is necessary to take account of their variation so as to obtain the relative abundance of the isomers from their observed intensity ratio.

The main contribution to f_v was assumed to be due to the torsional vibrational mode, the lowest among the vibrations of propene. The torsional frequency of propene is 193.6 cm⁻¹.[32] The torsional frequencies of the mono- and dideuterated methyl groups were calculated on the basis of isotopic shifts, and in our experiment, $kT = 142$ cm⁻¹; hence $f_v(CH_3)/f_v(CH_2D) = 1.0740$ and $f_v(CH_3)/f_v(CHD_2) = 1.1411$.[3a,33] The rotational constants[34,35] and the $1_{01} \leftarrow 0_{00}$ transition frequencies[32] for various isomers of propene are given in the literature. The dipole moment matrix element can be written as $\mu^2 S/(2J + 1)$, where S is the transition strength and μ is the molecular dipole moment active in the transition: μ_a is that in the $1_{01} \leftarrow 0_{00}$ transition. The values of μ_a for

(30) A. S. Esbitt and E. B. Wilson, Jr., *Rev. Sci. Instrum.*, **34**, 901 (1968).

(31) S. Saito, unpublished results.

(32) See footnote *a* in Table VI.

(33) Scharpen, *et al.*,[3b] used 1.074 as a relative factor of f_v for D_3 species and D_4 species at the temperature of 298 ± 2°K. However, the value, 1.074, is a relative factor of f_v at Dry Ice temperature.[3a]

(34) D. R. Lide, Jr., and D. Christensen, *J. Chem. Phys.*, **35**, 1374 (1961).

(35) E. Hirota and Y. Morino, *J. Chem. Phys.*, **45**, 2326 (1966).

the isotopic isomers were estimated from the dipole moment of normal species by calculating the rotation of the inertial axis with respect to the molecular frame due to the deuterium substitution. The width of the line, $\Delta\nu$, is not so different in the isomers of propene-d_1[3b] or propene-d_2 that $\Delta\nu$ was assumed to be constant within propene-d_1 isomers or propene-d_2 isomers. The effect of power saturation can be safely neglected under the experimental condition described above.

The correction coefficients for all the relevant pairs of various isomers are given in Table VII. The real relative concentration of each species was obtained by dividing the observed intensity ratio by the total correction coefficient listed in Table VII. The sum of the systematic and random errors was estimated to be several per cent of the relative concentration for each isomer.[3a]

We can determine the relative concentrations for the isomers of propene-d_1 and propene-d_2 whose partial pressure is as low as 0.1% of the total pressure. This is due to the high sensitivity of our microwave spectrometer, which can detect the line of $\gamma_{max} = 1 \times 10^{-10}$ cm^{-1}.[29]

Benzoylmethyl Radicals. Matrix Isolation Electron Spin Resonance Study[1]

Paul H. Kasai,*[2a] D. McLeod, Jr.,[2a] and Henry C. McBay*[2b]

Contribution from the Union Carbide Corporation, Tarrytown Technical Center, Tarrytown, New York 10591, and the Department of Chemistry, Morehouse College, Atlanta, Georgia 30314. Received March 30, 1974

Abstract: Phenacyl (= benzoylmethyl) radicals produced by photolysis and pyrolysis of phenacyl iodide were examined by matrix-isolation esr spectroscopy. While photolysis of the iodide trapped within the matrix produced phenacyl radicals of the normal structure (PhCOCH$_2$), the pyrolysis at 500° resulted in the formation of benzyl radicals suggesting intricate rearrangement and decomposition processes of the phenacyl radicals at elevated temperatures.
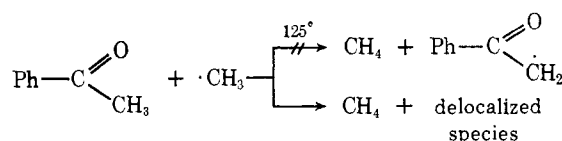
Sometime ago a technique was developed for the synthesis of 1,4-diketones[3a] *via* free-radical dehydrodimerization. In that work methyl free radicals generated by the thermal decomposition of diacetyl peroxide have been the hydrogen-abstracting agents. This technique has subsequently been used to synthesize several 1,4-diketones which are precursors of materials of possible biomedical interest.[3b] The technique dimerizes in good yield purely aliphatic ketones which have in their structure at least one hydrogen atom at the position α to the carbonyl group.

All attempts to dimerize by this technique alkyl phenyl ketones with the phenyl group attached directly to the carbonyl group have failed, however. Instead of the expected crystallizable 1,4-diketones, one repeatedly obtained amorphous, reddish-brown, resinous polymeric materials. Despite various attempts at its synthesis, nowhere in the literature has dibenzoylethane been reported as having been synthesized by free-radical coupling of phenacyl (= benzoylmethyl) radicals. These results suggest that the intermediate phenacyl radicals, if they exist, do not have the classical structure which would lead to the expected dimerization. Its real structure must have greatly reduced electron spin density at the α carbon. The attached benzoyl group might well serve as an electron sink enhancing delocalization of the spin density away from the α position.

Reported in this paper are the results of matrix isolation esr study of phenacyl radicals generated by photolysis and pyrolysis of phenacyl iodide. While the photolysis of the precursor isolated in an argon matrix at ~4°K produced the phenacyl radicals of "normal" structure, the pyrolysis of the iodide at 500° resulted in the formation of the benzyl radicals suggesting intricate rearrangement and decomposition processes of the phenacyl radicals at elevated temperature.

Experimental Section

The descriptions of the liquid-helium cryostat and X-band esr spectrometer system which allow the trapping of transient radicals in an inert gas matrix and the observation of their esr spectra have been reported earlier.[4] In the case of pyrolysis the precursor (phenacyl iodide) was passed through a resistively heated quartz tube and then trapped in an argon or neon matrix being formed upon a flat spatula-shaped sapphire rod. The sapphire rod is in contact with the liquid-helium reservoir and can be rotated about its long axis so that the direction of the magnetic field relative to the plane of the rod can be varied. In the case of photolysis, an argon matrix containing the precursor was first prepared and then irradiated with uv light through the side quartz window. A high-pressure mercury arc (GE, AH-6) equipped with a Corning 7-54 uv filter was used for this purpose. All the spectra were obtained while the matrix was maintained at liquid helium temperature, and the spectrometer frequency locked to the loaded sample cavity was 9.430 GHz.

(1) A part of the present study was done while H. C. McBay was at Tarrytown Technical Center as a Research Fellow during Summer 1968.

(2) Union Carbide Corp.; (b) Morehouse College.

(3) (a) M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Amer. Chem. Soc.*, 70, 1269 (1948); (b) H. C. McBay, unpublished results.

(4) P. H. Kasai, E. B. Whipple, and W. Weltner, Jr., *J. Chem. Phys.*, 44, 2581 (1966).