Catalysis by Organic Semi-conductors. The Photo-oxidation of Isopropyl Alcohol in the Liquid Phase

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Some organic catalytic reactions in biological systems, especially oxidation and reduction, have been explained recently by means of a concept of an organic semi-conductor,1) though no catalytic reaction of an organic semi-conductor has ever been studied *in vitro*. Zinc oxide, which is a typical n-type semi-conductor, is effective as a catalyzer for the oxidation of isopropyl alcohol to acetone with oxygen under ultraviolet-irradiation.2) On the other hand, it has been reported by many workers3) that some photo-oxidations of organic compounds with oxygen under ultraviolet or visible light irradiation are accelerated by various kinds of organic dyes, though there have not been many of the kinds of dye used as the catalyst for these photo-oxidations. Moreover, the property of a dye as an organic semi-conductor, chiefly the kind of charge-carrier, has been studied by Terenin4) and others5,6); some of their results are shown in Table I in the present paper. Here it is attempted to correlate the natures of organic semi-conductors with the catalytic ability of the dye used as a catalyzer for the

TABLE I. SIGN OF THE CHARGE CARRIERS

Dye	Meier5)	Terenin4)	Nelson6)
Crystal violet	n*	n	
Malachite green	n	n	n
Ethyl violet	n		
Methyl green	n		
Brilliant green	n	p	
Pinacyanole	n	n	n
Rhodamine B	n	n	
Auramine	n	p	
Erythrosine	p*		p
Eosine Y	p		
Acridine orange	p		
Rose bengal	p		
Congo red	p		
Kryptocyanine	p		n
Pyocyanine		n	
Floxine		p	
Chlorophylls		p	
Methyl-free phthalocyanine(Co^{2+}, Mn^{2+}, Fe^{2+}, Mg^{2+})		p	

* Sign of n or p means n- or p-type semi-conductor respectively.

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1) M. Calvin, *Rev. Mod. Phys.*, **31**, 147, 157 (1959).

2) G. M. Schwab, *Chem. Ber.*, **93**, 2755 (1960).

3) G. O. Schenck, *Naturwiss.*, **40**, 205, 229 (1953); K. Uchida, S. Kato and M. Koizumi, This Bulletin, **35**, 16 (1962).

4) A. Terenin, *Proc. Chem. Soc.*, **1961**, 321.

5) H. Meier, *Z. Wiss. Phot.*, **53**, 1 (1958).

6) N. Petruzzella and R. C. Nelson, *J. Chem. Phys.*, **37**, 3010 (1962).

photo-oxidation of isopropyl alcohol to acetone with oxygen under ultraviolet or visible light irradiation.

Experimental

Materials.—Isopropyl alcohol was purified by a fractional distillation after dehydration on calcium oxide. The dyestuffs used as the catalyzer, auramine, safranine T, fluorescein, eosine Y, crystal violet, malachite green, rhodamine B and brilliant blue, were of a commercial grade and had been purified by recrystallization or by extraction. Condensed aromatic or aza-aromatic hydrocarbons, such as anthracene, perylene, violanthrone, isoviolanthrone, phenazine, acridine and indanthrene, were also of a commercial grade and had been purified by sublimation or the recrystallization method.

The Measurement of the Reaction Rate.—The rate of the oxidation of isopropyl alcohol with oxygen was determined by measuring the amount of oxygen absorbed. To make a solution with a catalyzer in an appropriate concentration, a weighed amount of a catalyzer was dissolved or dispersed into 10 ml. of isopropyl alcohol which had been placed in a test tube of a common quantity (inner diameter, 15 mm.; thickness of the wall, 0.5 mm.). After oxygen had been bubbled in for 5 min., the test tube was connected with a gas burette, the air space of which had previously been filled with oxygen, and placed in a thermostat at a distance from the light source, which was placed in the same thermostat. The light source used was a 200 W. tungsten lamp or a Toshiba mercury lamp SHEL-100, which irradiates the waves at 2500, 3200, 3600, 4400, 5500 and 5800 Å.

Analysis of the Acetone and Pinacol Produced.—The acetone and the pinacol formed in the reaction mixture, after they had cooled in dry ice, were analyzed with a gas chromatograph, Hitachi KGL-2, in which polyethylene glycol was used as an adsorbent and hydrogen gas as a carrier gas.

Results and Discussion

The Effects of Dyes on the Rate of Oxygen Absorption.—As is shown in Fig. 1, the amount of oxygen absorbed increased linearly with the reaction time after a certain induction period, no matter what kind of dye was chosen as the catalyzer. However, the absorption rates differed from dye to dye. They may be classified into two groups, one group with a large rate, and another group with a small rate. All the catalyzers which afford the large rate are the dyes which were identified as p-type semi-conductors by Terenin, while those which afford the small rate are ones which were identified as n-type semi-conductors by the same author. Although the magnitude of the induction period of each of the oxidations catalyzed by p-type dyes was not the same, all the inclinations of the straight lines in Fig. 1 are parallel and are also parallel to that of the oxidation which proceeded without a dye. As Table II shows, the p-type dyes were gradually decolorized during the reaction and the decolorized dyes may not be effective in accelerating the production of hydrogen peroxide. Therefore, the curves of the oxygen absorption rate must have the same inclination after the induction period as in an oxidation without a dye. This means that the oxidation is a chain reaction carried out by means of the hydrogen peroxide which is produced by the reaction of dyes, isopropyl alcohol and oxygen, and p-type dyes are effective merely in producing hydrogen peroxide. On the other hand, the n-type dyes must not be effective in producing hydrogen peroxide.

The second remarkable difference between the reaction with an n-type dye and that with a p-type dye is the molar ratio of the acetone formed to the oxygen absorbed. As Table III

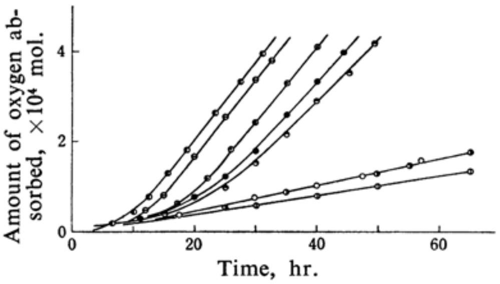

Fig. 1. Effects of dyes on the rate of the oxygen absorption: Light source; 100 W. mercury lamp, irradiated distance; 10 cm., irradiated temp.; 43～44°C, concn.; 5×10^{-4} mol./l. and reaction vessel; Pyrex glass. ◐ Blank, ⊖ eosine Y, ⊙ auramine, ● fluorescein, ◓ safranine T, ◐ rhodamine B, ○ crystal violet, and ⦶ brilliant blue.

TABLE II. DECOLORATION OF DYES*

Dye	Irradiated time, hr.	Decoloration, %
Fluorescein	30	82.8
Eosine Y	15	68
	24	97.4
Safranine T	19	6.5
	38	15.2
	43	28.6
Auramine	19～20	22.9
Rhodamine B	40	1.6
Crystal violet	40	1.8
Malachite green	27	58.2
	57～60	80.3

* Light source; 100 W. mercury lamp, concentration of dye; 5×10^{-4} mol./l. and irradiated distance; 10 cm.

TABLE III. RELATION BETWEEN OXYGEN ABSORBED AND ACETONE FORMED (IN THE CASE OF DYE)[*1]

Exp. No.	Dye	Irradiated distance cm.	Temp. °C	Time hr.	Amount of O_2 absorbed $\times 10^4$ mol.	Amount of acetone formed $\times 10^4$ mol.	Ratio[*2]
1	Fluorescein	10	42∼43	46	3.89	7.74	1.93
2	Safranine[*3] T	10	42∼43	47.7	4.81	7.84	1.63
3	Eosine Y	10	43	30.4	3.52	5.66	1.61
5	Auramine	10	44	46.8	5.95	7.02	1.17
6	Crystal violet	10	43∼44	67.0	2.07	0.10	0.05
7	Crystal violet	5∼6	30	21.3	1.1	0.7	0.64
8	Crystal violet[*3]	10	43∼44	94.5	3.23	2.10	0.65
9	Rhodamine B[*3]	10	43∼44	67.6	2.3	0.57	0.25
10	Rhodamine B[*3]	5∼6	30	20.7	1.00	0.79	0.79
11	Malachite green	5∼6	30	27.3	0.98	0.55	0.56
12	Brilliant blue	5∼6	30	21.4	0.49	0.35	0.72
13	Eosine Y-Rhodamine[*4] B	5∼6	30	4.9	0.44	0.40	0.90
14	Eosine Y-Rhodamine[*4] B	5∼6	30	19.5	1.00	1.27	1.27
15	Blank	10	43∼44	32.3	4.4	7.15	1.63

[*1] Light source; 100 W. mercury lamp, concentration of dye; $5\sim10^{-4}$ mol./l. except Exp. Nos. 2, 8, 9 and 10. Reaction vessel; Pyrex glass tube.

[*2] Ratio is the molar ratio of the acetone formed to the oxygen absorbed.

[*3] The concentration of dye: Exp. Nos. 2, 8 and 9; 2.5×10^{-4} mol./l., Exp. No. 10; 8×10^{-4} mol./l.

[*4] Eosine Y: 5×10^{-4} mol./l., rhodamine B: 5×10^{-4} mol./l.

shows, the p-type dyes afforded a ratio larger than unity, while the n-type dyes afforded a ratio less than unity. Even when the crystal violet of an n-type dye was used as the catalyzer and the reaction system was irradiated at a nearer distance, 5∼6 cm., from a light source, the amount of the acetone formed was yet very little.

Furthermore, it was astonishing that the reaction catalysed by a p-type dye produced mainly acetone, while that catalyzed by an n-type dye produced pinacol. The irradiation of isopropyl alcohol in an atmosphere of oxygen in the presence of crystal violet at the distance of 5∼6 cm. from the light source for 210 hr. at 40∼50°C produced about 7×10^{-4} mol. of pinacol per 10 ml. of isopropyl alcohol. Under the same conditions, eosine Y of a p-type produced only about 1.05×10^{-4} mol. of pinacol per 10 ml. of isopropyl alcohol, even after irradiation for two weeks.

The Effects of the Mixed Dyes on the Oxygen Absorption.—Eosine Y (a p-type dye) and rhodamine B (an p-type dye) were used together as the catalyzers of the oxidation, because it was expected that a combination of a p-type catalyzer and an n-type catalyzer might be effective because synergitic. Since the visible absorption spectrum of these mixed dyes was the sum of the absorption spectra of eosine Y and rhodamine B, it seems that there is no molecular interaction between eosine Y and rhodamin B in isopropyl alcohol.

As is shown in Figs. 2 and 3, the rate of oxygen absorption increased with the increase in the concentration of eosine Y at a constant concentration of rhodamine B; on the other hand, it did not vary with an increase in the concentration of rhodamine B at a constant concentration of eosine Y. This means that, contrary to our expectations, there was no synergitic action, even when two kinds of dyes were mixed. While the oxygen absorbed-reaction time curve rose steeply at the beginning of the reaction, as Fig. 2 shows, the inclination of the curve decreased gradually and at the final stage of the reaction approached

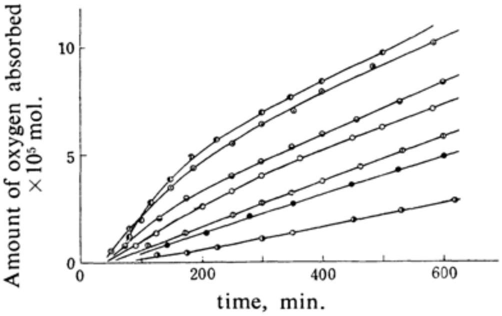

Fig. 2. Effects of the mixed dyes on the oxygen absorption (at the constant concentration of rhodamine B): Irradiated distance; 5∼6 cm., irradiated temp.; 30°C, and reaction vessel; Pyrex glass.
Concn. of rhodamine B; ◐ 5×10^{-4} mol./l.
Eosine Y; ◐ 12×10^{-4} mol./l., ⊙ 10×10^{-4} mol./l., ◒ 7×10^{-4} mol./l., ○ 6×10^{-4} mol./l., ① 5×10^{-4} mol./l., ● 3.5×10^{-4} mol./l.

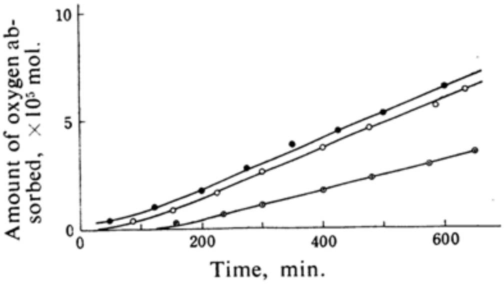

Fig. 3. Effects of the mixed dyes on the oxygen absorption (at the constant concentration of eosine Y): Condition of irradiation was same to Fig. 2.
Eosine Y; 5×10^{-4} mol./l. Rhodamine B; ○ 5×10^{-4} mol./l., ● 10×10^{-4} mol./l. ⊙ Rhodamine B alone; 5×10^{-4}mol./l.

the inclination of that curve obtained with rhodamine B alone. This fact could be explained as follows. When eosine Y was used as the catalyzer together with rhodamine B, eosine Y was also decolorized gradually as much as 67.7% after 450 min. and 79% after 1168 min.; consequently, the oxidation rate was retarded.

The Effects of Dyes on the Rates of the Formation of Acetone.—When isopropyl alcohol was irradiated in an atmosphere of oxygen at 17∼18°C for 20 hr. with a 200 W. tungsten lamp placed 15 cm. from the vessel, no acetone was detected. However, when a p-type dye was present in this system, acetone was produced, while, except for rhodamine B, no n-type dyes were effective (Fig. 4). Now, the rate of the formation of acetone was measured under the reaction conditions just cited. As is clear from the results shown in Fig. 5, each dye has its optimum concentration at which the maximum rate was exhibited: eosine Y, 8×10^{-4} mol./l.; fluorescein; 7.5×10^{-4}; auramine and safranine T, $0.05\sim0.5\times10^{-4}$ mol./l., and rhodamine B, 0.08×10^{-4} mol./l. The order of the magnitude of these optimum concentrations was the same as that indicated in Fig. 1.

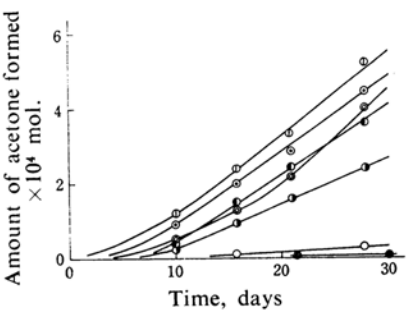

Fig. 4. Catalytic action of dyes: Light source; 200 W. tungsten lamp, irradiated distance; 15 cm., temp.; 17∼18°C, and reaction vessel; Pyrex glass.
⊙ Eosine Y; 5×10^{-4} mol./l., ◎ fluorescein; 5×10^{-4} mol./l., ① auramine; 0.1×10^{-4} mol./l., ◑ safranine T; 0.1×10^{-4} mol./l., ◐ rhodamine B; 0.1×10^{-4} mol./l., ● brilliant blue, crystal violet; 5×10^{-4} mol./l. and ○ without dye.

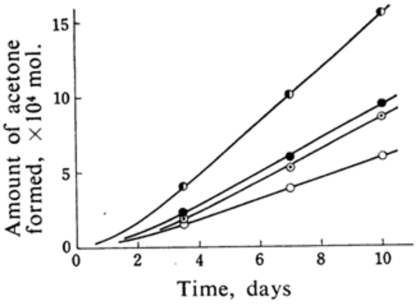

Fig. 5. Effect of the concentration of eosine Y to catalytic action: Irradiated distance; 17 cm., temp.; 39∼42°C and light source; 200 W. tungsten lamp.
Concn. of eosine Y; ● 10×10^{-4} mol./l., ◐ 7.5×10^{-4} mol./l., ⊙ 5.0×10^{-4} mol./l., ○ 1.0×10^{-4} mol./l.

The Effects of Condensed Aromatic and Aza-aromatic Hydrocarbons.—An oxidation catalyzed by a condensed aromatic or aza-aromatic hydrocarbon was carried out in the presence of rhodamine B, which may be effective in suppressing the effects of hydrogen peroxide, and also, if necessary, in the presence of sodium palmitate, with which an insoluble aromatic hydrocarbon could be dispersed. The other experimental conditions were the same as those holding in the cases of dyes. As is clear from the results shown in Fig. 6, the compound

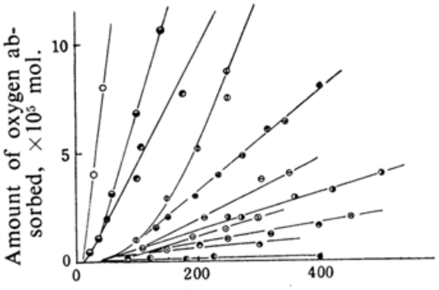

Fig. 6. Effects of aromatic and aza-aromatic hydrocarbons on the rate of the oxygen absorption: Condition of irradiation; same to Table IV. ① Anthracene; 5×10^{-4} mol./l., ⊖ pyrene; 2 mg., ◒ phenazine; 5×10^{-4} mol./l., ○ anthraquinone; 5×10^{-4} mol./l., ◑ perylene; 10^{-3} mol./l., ◐ violathrone; 2.3 mg., ● isoviolanthrone; 2.8 mg., ◓ indanthrene; 2 mg., ⊗ fluoridine; 3.0 mg., ◩ triphenodioxazine; 3 mg., ⊕ rhodamine B alone; 5×10^{-4} mol./l., ⊙ rhodamine B and sodium palmitate; 5×10^{-4} mol./l.

TABLE IV. RELATION BETWEEN OXYGEN ABSORBED AND ACETONE FORMED (IN THE CASE OF CONDENSED AROMATIC AND AZA-AROMATIC HYDROCARBONS)[*1]

Compound	Irradiated time hr.	Amount of O_2 absorbed $\times 10^4$ mol.	Amount of acetone formed $\times 10^4$ mol.	Ratio
Anthracene	6.05	1.71	2.2	1.29
Acridine	7.21	1.64	—	—
Phenazine	2.9	1.34	1.47	1.09
Anthraquinone	2.53	1.8	3.93	2.18
Pyrene	7.61	0.61	0.4	0.65
Perylene	7.06	0.34	0.41	1.2
Fluoridine[*2]	5.1	0.67	—	—
Triphenodioxazine[*2]	5.18	0.07	0	0
Indanthrene[*2]	5.08	0.43	0.06	0.14
Violanthrone[*2]	6.73	0	—	—
Isoviolanthrone[*2]	2.6	0	—	—

*1 Reaction was carried out in the presence of rhodamine B. The concentration of each compound was 5×10^{-4} mol./l., that of rhodamine B being equivalent.
Irradiated distance: 5～6 cm. Temperature: 30°C

*2 This compound was dispersed by sodium palmitate.

TABLE V. RELATION BETWEEN THE CATALYTIC ABILITY AND THE CONDUCTIVE PROPERTY OF ORGANIC SEMI-CONDUCTORS

Compound	Catalytic ability[*1]	Type of conductivity[*2]	Compound	Catalytic ability	Type of conductivity
Eosine Y	+	p	Anthracene	+	p
Safranine T	+	p	Acridine	+	p
Auramine	+	p	Phenazine	+	p
Fluorescein	+	p	Pyrene	+	p
			Fluoridine	+	p
Crystal violet	−	n	Triphenodioxazine	−	n
Rhodamine B	+	n	Indanthrene	−	n
Malachite green	−	n	Violanthrone	−	n
Brilliant blue	−	n	Isoviolanthrone	−	n

*1 Sign of + means to have cataltic action, and sign of − means not to have it.

*2 B. Rosenberg, *J. Chem. Phys.*, **29**, 1108 (1958); ibid., **37**, 1371 (1962); H. Inoue, K. Noda and E. Imoto, This Bulletin, in press; Literature, 4, 5 and 6, described in this paper.

containing a few condensed benzene rings and a heteroatom is rather more effective than a compound containing many condensed benzene rings. It is uncertain whether this is caused by the difference between the dispersed and dissolved states of the catalyzer, or, substantially, by the difference in the excited energies. As Table IV shows, the molar ratio of the acetone produced to the oxygen absorbed was larger than unity. p-Type compounds were effective, but n-type compounds ineffective, similar to the cases of dyes. Furthermore, a compound which can easily take its triplet state seemed to be more effective. For example, phenazine, the density of the triplet of which was 10^3 larger than that of anthracene, was more effective than anthracene.

An Assumed Mechanism of the Sensitized Photo-oxidation of Isopropyl Alcohol.—Electrical conductivity is a property which should be attributed to a solid aggregate of molecules, and the catalytic action of a dye in a solution must result from the property of an isolated molecule. In spite of this inconsistency, the fact that electrical conductivity is very dependent on properties of the molecule itself has allowed us to classify dyes into two groups according to the type of electrical conductivity. As has been described above and as is summarized in Table V, p-type compounds are generally effective as a sensitizer of the photo-oxidation of isopropyl alcohol with oxygen, while n-type compounds are ineffective. Compounds containing a heteroatom are particularly effective. p-Type conductivity has been explained by Rosenberg7) as the trapping of an excited electron at a triplet state, whereupon the hole formed migrates to an electrode. A hetero-

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(7. B Rosenberg, *J. Chem. Phys.*, **37**, 1371 (1962).

aromatic compound may be easily excited to its triplet state, as has been found true of quinoline and phenazine. In a heteroaromatic compound excited to a triplet state, an excited electron may be trapped and a hole may migrate to another compound. The migration of a hole from one compound to another compound means an oxidation. Now, the sensitized photo-oxidation of isopropyl alcohol with oxygen to acetone may proceed at first by the migration of a hydrogen atom of isopropyl alcohol to an excited p-type sensitizer. The formation of DH_2 by some reaction, for example, by reaction 3 or 4, involves the decoloration of the dye.

$$D \rightarrow D^* \tag{1}$$

$$(CH_3)_2CHOH + D^* \rightarrow (CH_3)_2\dot{C}OH + HD\cdot \tag{2}$$

$$(CH_3)_2CHOH + HD\cdot \rightarrow (CH_3)_2\dot{C}OH + H_2D \tag{3}$$

$$(CH_3)_2\dot{C}OH + HD\cdot \rightarrow (CH_3)_2CO + H_2D \tag{4}$$

Though the mechanism of the formation of hydrogen peroxide is not certain and is not within the scope of this paper, hydrogen peroxide must be produced from some radicals, such as HD· (5 and 6).

$$HD\cdot + O_2 \rightarrow D + HO_2\cdot \tag{5}$$

$$(CH_3)_2CHOH + HO_2\cdot \rightarrow (CH_3)_2\dot{C}OH + H_2O_2 \tag{6}$$

When a molecule of hydrogen peroxide is produced, it must oxidize a molecule of isopropyl alcohol to acetone by the following chain reactions (7—11), though this mechanism is merely speculative. This must also be the reason why the molar ratio of the acetone produced to the oxygen absorbed was larger than unity.

$$H_2O_2 \rightarrow HO\cdot + \cdot OH \tag{7}$$

$$(CH_3)_2CHOH + \cdot OH \rightarrow (CH_3)_2\dot{C}OH + H_2O \tag{8}$$

$$(CH_3)_2\dot{C}OH + O_2 \rightarrow (CH_3)_2CO + HO_2\cdot \tag{9}$$

$$(CH_3)_2CHOH + HO_2\cdot \rightarrow (CH_3)_2\dot{C}OH + H_2O_2 \tag{10}$$

$$(CH_3)_2\dot{C}OH + \cdot OH \rightarrow (CH_3)_2CO + H_2O \tag{11}$$

$$2(CH_3)_2CHOH + O_2 \rightarrow 2(CH_3)_2CO + 2H_2O$$

On the other hand, since a photo-excited sensitizer of the n-type could not abstract a hydrogen atom from isopropyl alcohol, it was ineffective as the catalyzer. The radical, $(CH_3)_2\dot{C}OH$, which is necessary for the formation of pinacol may be produced directly from isopropyl alcohol and oxygen.

Summary

The natures of organic semi-conductors have been correlated with the catalytic ability for the photo-oxidation of isopropyl alcohol to acetone with oxygen under ultraviolet or visible light irradiation. p-Type compounds are generally effective as sensitizers, but n-type compounds are ineffective. Heteroaromatic compounds are more effective than the parent aromatic compounds among p-type compounds. The molar ratio of the acetone formed to the oxygen absorbed is larger than unity in the case of p-type compounds and less than unity in the case of n-type compounds. Finally, it has been assumed that the migration of a positive hole in a p-type compound can be correlated with the migration of a hydrogen atom of isopropyl alcohol.

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