Hydrogen Isotope Exchange in *ortho*-Alkyl-phenyl Ketones Mediated by Illuminated Semiconductor Powders[1]

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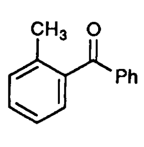
Photocatalysed hydrogen isotope exchange between *o*-methylbenzophenone, o-methylacetophenone or 5,8-dimethyl-α-tetralone and deuterium or tritium labelled alcohols has been studied in suspensions containing inorganic semiconductors (CdS, ZnO and TiO_2). It has been shown that adsorption of the ketone onto the semiconductor surface is necessary for the exchange reaction to occur. The influence of the electron scavenger (CBr_4 and O_2) and the hole scavenger (1,3,5-trimethoxybenzene) on the reaction yield has been examined. A mechanism of the studied reaction is proposed.

Recently studied photochemical reactions involving electron transfer at semiconductor surfaces have been focused on synthetic as well as on solar energy conversion problems and a number of comprehensive reviews on this subject have been published.[2] Various reactions of organic molecules such as dimerization,[3] geometrical isomerization,[4] valence isomerization,[4f,g,5] cycloreversion,[3a,4fg,5b] sigmatropic rearrangement[5b,6] as well as oxidation and reduction[7] have been catalysed by illuminated semiconductor powders. In all the above-mentioned reactions the involvement of radical cations formed by the electron transfer from organic molecules to photogenerated holes in the valence band of the semiconductor has been demonstrated.

We have recently shown that various *o*-methyl substituted phenyl ketones upon ionization spontaneously tautomerize to form the corresponding reactive radical cations of enols.[8] On the other hand we have pointed out that hydrogen isotope exchange can be successfully applied to probe the formation of transient neutral photoenols from various *o*-methyl substituted phenyl ketones.[9]

Although various reactions of organic compounds catalysed by excited semiconductors have been widely investigated the hydrogen isotope exchange reaction had never been previously reported. In the present studies we decided to apply hydrogen isotope exchange as a model reaction to test the reactivity of enol radical cations generated photocatalytically on semiconductor surfaces. Herein we report the results of our studies on the photocatalysed hydrogen–deuterium and hydrogen–tritium exchange between *o*-methylbenzophenone (**1**), *o*-methylacetophenone (**2**) or 5,8-dimethyl-α-tetralone (**3**) and labelled alcohols in suspensions containing in organic semiconductors (Cds, ZnO and TiO_2).



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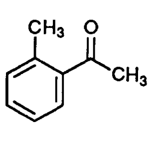

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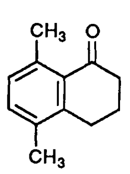

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Experimental

Materials.—*o*-Methylbenzophenone (**1**) (Aldrich) and *o*-methylacetophenone (**2**) (Aldrich) were used without further purification. 5,8-Dimethyl-α-tetralone (**3**) was synthesized from *p*-xylene using a procedure adopted from that described for 2,5,8-trimethyl-α-tetralone.[10] High-purity CdS, ZnO and TiO_2 (99.999%) were obtained from Aldrich. Deuteriated methanol ($CH_3O[^2H]$) (OPIDI, Poland—isotopic purity 99.5%) was used. Tritiated methanol ($CH_3O[^3H]$) (49.25 MBq mol^{-1}) and isopropyl alcohol ($Pr^iO[^3H]$) (408.25 MBq mol^{-1}) were prepared by hydrogen–tritium exchange with tritium labelled water ($[^3H]_2O$) (OPIDI, Poland) and dried by the standard procedure. Methylene chloride (Merck) and acetonitrile (Apolda) were dried by the standard procedure.

Irradiation and Product Analysis.—The studied reaction was performed in a quartz tube containing the ketone (0.3 mol dm^{-3}; 3 cm^3) in labelled alcohol (or in a mixture of alcohol with methylene chloride or acetonitrile) and semiconductor (50 mg). The solution was irradiated with a high-pressure mercury lamp (Narva, 200 W) through a 357 nm cut-off filter (Oriel) and was constantly stirred during the irradiation. After the irradiation the semiconductor was filtered off and the labelled ketone was separated from the reaction mixture by thin-layer chromatography. The extent of incorporation of deuterium into the methyl group of ketone was analysed by MS (Hewlett-Packard HP-5970 MSD mass spectrometer). The radioactivity of tritium labelled ketone was measured with a liquid scintillation counter (LKB Wallac 1219 Rackbeta) using a solution of butyl-PBD (2-biphenyl-4-yl-5-phenyl-1,3,4-oxadiazole) (Koch-Light) (8 g dm^{-3}) in dioxane as scintillator.

Measurements of Ketone Adsorption on the Semiconductor Surface.—The amount of ketone adsorbed on a semiconductor surface was determined by static adsorption measurements analysing spectrophotometrically the concentration of ketone solution before and after contact with the semiconductor.

Calculation of Reaction Yield.—In all experiments the irradiation time was as short as sufficed to secure a precise quantitative analysis of labelled ketone. The amount of deuterium or tritium incorporated into ketone molecules was always proportional to the irradiation time. Also no side-product was noticed. The yield of the studied hydrogen–tritium isotope exchange reaction was calculated from eqn. (1), where a_k = molar tritium radioactivity of the ketone related to one

$$\omega = \frac{a_k}{a_{eq}} \times 100\% \qquad (1)$$

C–H bond of the *o*-methyl group, *i.e.* one-third of the total molar tritium radioactivity, and a_{eq} = equilibrated molar tritium radioactivity of the alcohol. The value of a_{eq} was obtained from eqn. (2), where a_a^0 = initial molar tritium

$$a_a^0 \times n_a = a_{eq}(3n_k + n_a) \qquad (2)$$

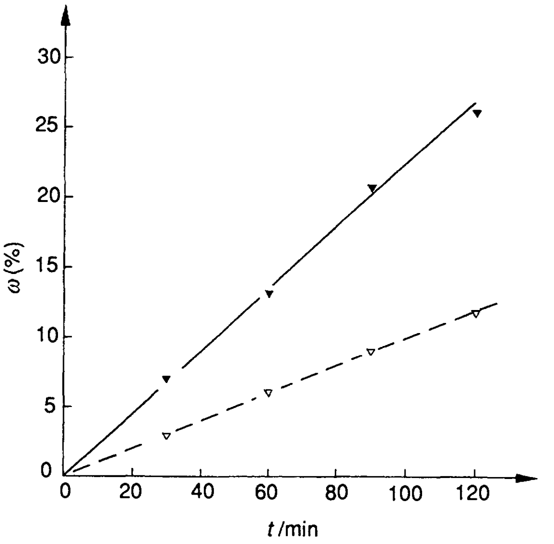


Fig. 1 The yield (%) of photocatalysed hydrogen isotope exchange reaction between **1** and MeO[^{3}H] (dashed line) or Pr^{i}O[^{3}H] (solid line) as a function of irradiation time

Table 1 The yield of photocatalysed hydrogen isotope exchange between *o*-methylbenzophenone (**1**), *o*-methylacetophenone (**2**) or 5,8-dimethyl-α-tetralone (**3**) and labelled alcohols in semiconductor suspensions^a

Compound	Solvent	Semiconductor		
		CdS^b	ZnO^c	TiO$_2$^{d}
1	$CH_3O[^3H]$	11.8^e	11.1^e	11.1^e
		8.6^f	10.1^f	9.5^f
	$CH_3CN + CH_3O[^3H]$ (9:1)	9.1^e	8.9^e	8.7^e
		6.2^f	7.3^f	8.5^f
	$CH_2Cl_2 + CH_3O[^3H]$ (9:1)	16.6^e	13.9^e	13.2^e
		13.3^f	8.5^f	11.6^f
	$CH_3O(^2H)$	26.8^e	20.5^e	22.4^e
	$Pr^iO[^3H]$	26.1^e	17.6^e	17.7^e
		16.6^f	13.7^f	14.7^f
	$CH_3CN + Pr^iO[^3H]$ (9:1)	24.3^e	26.3^e	14.7^e
		12.7^f	20.2^f	8.4^f
2	$Pr^iO[^3H]$	5.1^e	2.4^e	2.1^e
		2.8^f	2.0^f	1.5^f
	$CH_3CN + Pr^iO[^3H]$ (9:1)	2.5^e	1.4^e	1.6^e
		1.9^f	1.3^f	1.4^f
3	$Pr^iO[^3H]$	1.5^e	1.6^e	1.2^e
		1.2^f	1.3^f	0.9^f

[a] In % after 120 min of irradiation; measurements done at room temp. for solutions containing 50 mg of semiconductor in 3 cm^3. [b] Aldrich, 99.999%, 3.1 m^2 g^{-1}. [c] Aldrich, 99.999%, 8.4 m^2 g^{-1}. [d] Aldrich, 99.999%, 6.0 m^2 g^{-1}. [e] Argon-saturated solution. [f] Aerated solution.

radioactivity of alcohol, n_a and n_k = number of moles of alcohol and ketone, respectively.

The yield of hydrogen–deuterium exchange is represented as a fractional population of deuteriated molecules (fractions of CH_2D, CHD_2 and CD_3 were taken into account).

Results and Discussion

An example of the observed relationship between the reaction yield and the irradiation time is shown in Fig. 1. Since we monitored the early stages of the hydrogen isotope exchange reaction, being far from the equilibrium, this relationship can be approximated by a straight line. In order to compare quantitatively the reaction yields obtained under various experimental conditions we will treat the reaction yield after 120 min of irradiation as a standard value for comparison in all experiments. The results of photocatalysed hydrogen isotope exchange reaction between *o*-alkyl phenyl ketones **1**, **2** and **3** and labelled alcohols in the semiconductor suspensions are collected in Table 1. The studied reaction has not been observed in the dark in the presence of semiconductor. As can be seen in Table 1 the yield of exchange reaction for **1** is higher in solvents of lower polarity. In the case of *o*-methylacetophenone (**2**) the studied reaction was less effective as compared to **1** and was observed in isopropyl alcohol and in a mixture of isopropyl alcohol with acetonitrile. For 5,8-dimethyl-α-tetralone (**3**) the reaction was only observed in isopropyl alcohol. The exchange reaction both for **2** and **3** was not effective in methanol. All the above-mentioned observations inclined us to study the influence of adsorption of ketone on the semiconductor surface on the reaction yield. The amounts of ketone **1**, **2** and **3** adsorbed on the semiconductor surface in the studied systems are tabulated (Table 2). We can see very clearly that for *o*-methylbenzophenone (**1**) a larger amount of ketone molecules is adsorbed on the semiconductor surface in less polar solvents. For **2** and **3** in methanol or in a mixture of methanol with methylene chloride or acetonitrile and for **3** in a mixture of isopropyl alcohol with acetonitrile, no adsorption of ketone molecules on the semiconductor surface was observed. Correlation between the reaction yield and the amount of *o*-methylbenzophenone (**1**) adsorbed on CdS, ZnO or TiO$_2$ surface is presented in Fig. 2. The results of static adsorption measurements enable us to conclude that adsorption of ketones on the semiconductor surface is necessary for the exchange reaction to occur.

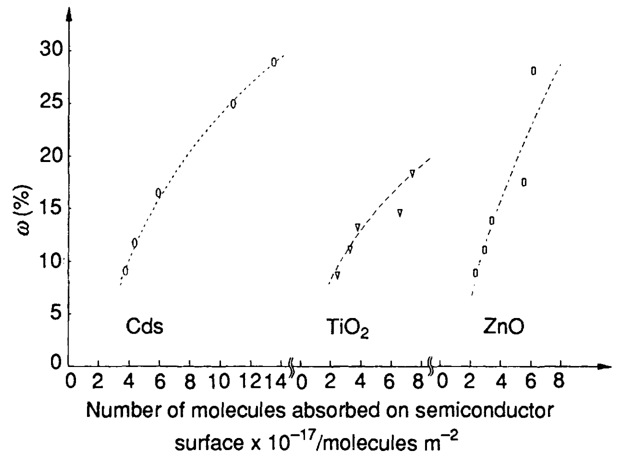


Fig. 2 The yield (%) of photocatalysed hydrogen isotope exchange reaction between **1** and labelled alcohols in semiconductor suspensions as a function of the amount of ketone adsorbed on semiconductor surface

The results presented in Table 1 also show that the measured yield of reaction is higher in the absence of oxygen (argon-saturated solution). Until now the presence of oxygen (a good electron scavenger which traps the excited electron as superoxide ion $O_2^{\bullet -}$, thereby prolonging the lifetime of the valence band hole by delaying the collapse of the electron-hole pair) was thought to enhance the reaction rate in the studied reaction.[3a–e,5a–d] Only Al-Ekabi and de Mayo[4a] for photocatalysed *cis–trans* isomerization of a simple olefin in the presence of CdS and Ikezawa and Kutal[5e] for valence isomerization of quadricyclane mediated by illuminated CdS or TiO$_2$ powders have reported that in the presence of oxygen the yield of the studied reaction decreases. According to Al-Ekabi and de Mayo's explanation,[4a] oxygen competes with the organic substrate for active sites on the semiconductor surface, or electron donation to the photogenerated hole by chemisorbed oxygen competes with oxidation of the substrate and for that

Table 2 The molar fraction (%) of ketone **1**, **2** and **3** adsorbed on a semiconductor surface in various solvents[a]

Compound	Solvent	Semiconductor		
		CdS	ZnO	TiO_2
1	CH_3OH	4.5	8.2	6.5
	$CH_3CN + CH_3OH$ (9:1)	3.9	6.5	4.9
	$CH_2Cl_2 + CH_3OH$ (9:1)	6.0	9.5	7.5
	Pr^iOH	13.9	15.3	14.7
	$CH_3CN + Pr^iOH$ (9:1)	11.1	17.0	13.0
2	CH_3OH	—	—	—
	Pr^iOH	4.0	4.8	4.3
	$CH_3CN + Pr^iOH$ (9:1)	3.8	5.4	4.0
3	CH_3OH	—	—	—
	Pr^iOH	5.9	7.5	6.4
	$CH_3CN:Pr^iOH$ (9:1)	—	—	—

[a] Measurements done at room temp. for solutions ($c_{ket} = 0.0001$ mol dm^{-3}) containing 10 mg of semiconductor in 5 cm^3.

Table 3 The yield of photocatalysed hydrogen isotope exchange reaction between **1**, **2** and **3** and labelled alcohols in CdS suspension in the presence or absence of added electron acceptor or donor[a]

Compound	Added substance (mol dm^{-3})	Solvent	Yield (%)
1	—	$Pr^iO[^3H]$	26.1
	CBr_4 (0.002)	$Pr^iO[^3H]$	36.3
	CBr_4 (0.003)	$Pr^iO[^3H]$	39.0
	CBr_4 (0.004)	$Pr^iO[^3H]$	44.3
	Naphthalene (0.005)	$Pr^iO[^3H]$	18.4
	Naphthalene (0.010)	$Pr^iO[^3H]$	13.7
	—	$CH_3O[^3H]$	11.8
	1,3,5-Trimethoxybenzene (0.004)	$CH_3O[^3H]$	8.7
2	—	$Pr^iO[^3H]$	5.1
	CBr_4 (0.004)	$Pr^iO[^3H]$	10.1
3	—	$Pr^iO[^3H]$	1.5
	CBr_4 (0.004)	$Pr^iO[^3H]$	2.6

[a] In % after 120 min of irradiation; measurements done at room temp. for argon-saturated solutions containing 50 mg of CdS in 3 cm^3.

reason the observed reaction yield is lower. Ikezawa and Kutal[5e] explained the lower yield of the studied reaction in the presence of oxygen as a result of rapid reverse electron transfer from $O_2^{\bullet -}$ to the radical cation of the substrate at the semiconductor surface.

In our opinion in the case studied by us, the hydrogen isotope exchange reaction, another explanation is also possible. Reaction between the radical cation of the substrate (in keto or enol form) and oxygen could cause lowering of the reaction yielded (a similar reaction has recently been postulated).[11] In experiments with solutions containing oxygen, a trace of a side-product was evidenced on the chromatography plate. Unfortunately we were not able to characterize this product and it is likely to have been formed by oxygenation of substrate radical cations.

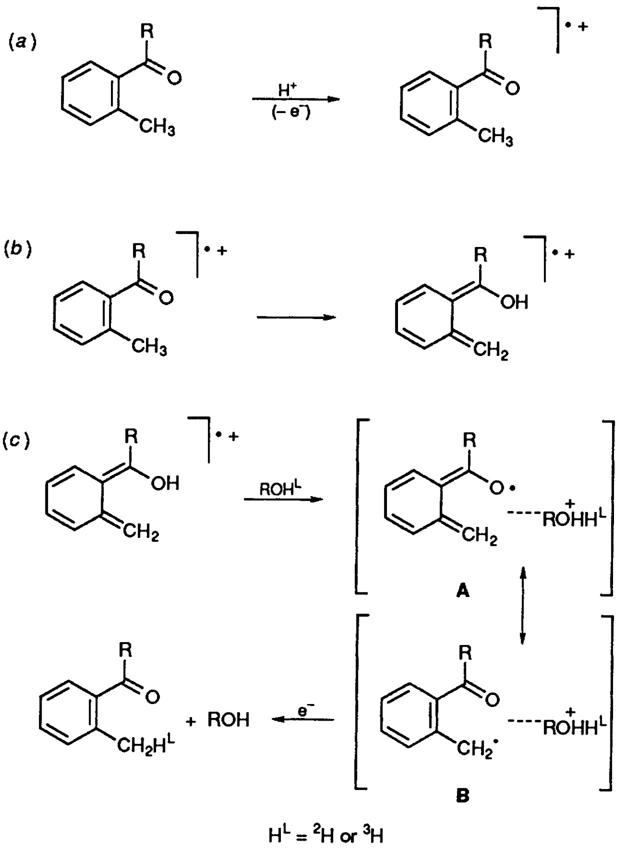
It was also found (as we expected) that addition of CBr_4 (which acts as an electron acceptor)[4f] increases the reaction yield (Table 3). To look for evidence of the involvement of radical cations in an isotope exchange reaction, studies on the influence of the hole scavenger on reaction yield were also undertaken. Oxidation potentials of the studied ketones **1**, **2** and **3**, naphthalene and 1,3,5-trimethoxybenzene are compared in Table 4. It was found that addition of naphthalene or 1,3,5-trimethoxybenzene sharply decreased the reaction yield (Table 3).

In the presence of the hole scavenger the photocatalysed exchange reaction can be retarded as a result of neutralization of the substrate radical cation by electron transfer from the hole scavenger. Quenching of the exchange reaction by the electron donors demonstrates an involvement of the radical cations as intermediates in the observed hydrogen isotope exchange.

In order to prove that radical cations participate in the reaction of hydrogen isotope exchange and to eliminate a possible participation of ketone molecules in the excited states in the reaction mechanism, which could be formed by neutralization of substrate radical cations, the studies with 5,8-dimethyl-α-tetralone (**3**) were performed. Electronic excitation of ketone molecules can result in the formation of neutral enols,[12] which could also participate in the hydrogen isotope exchange reaction. Such a reaction involving neutral enols was not observed for **3**, where only an enol in the *Z*-configuration can be formed,[9a] whose lifetime is too short to exchange hydrogens.[13] A measurable value of reaction yield noticed for the hydrogen isotope exchange in **3** (Tables 1 and 3) seems to rule out participation of neutral enols in hydrogen exchange processes.

The measured value of the kinetic isotope effect k_D/k_T in labelled methanol for **1** was found to be 2.27, 1.84 and 2.07, respectively, for CdS, ZnO and TiO_2, indicating that hydrogen atom transfer is involved in the rate-determining step.

A proposed mechanism of the studied hydrogen isotope exchange reaction is shown in Scheme 1. In this mechanism, the radical cation generated in the reaction (*a*) in Scheme 1 spontaneously tautomerizes [reaction (*b*) in Scheme 1] to form the enol radical cation.[8] Subsequent proton transfer to the alcohol molecule gives a transient radical-ion complex. A similar reaction is observed during radiolysis of alcohols.[14] Charge redistribution in the radical giving a more stable benzyl-type radical [in the second step of reaction sequence (*c*) in



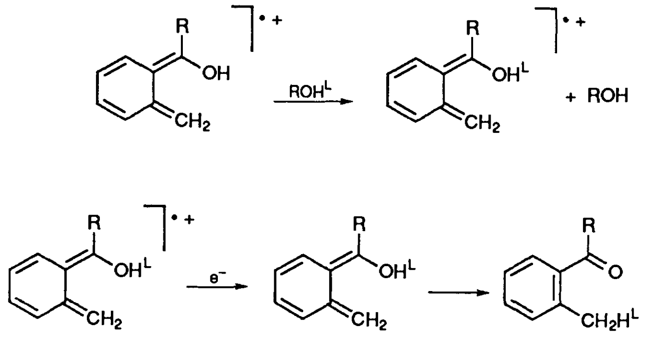
Scheme 1

Table 4 Oxidation potentials *vs.* SCE in acetonitrile

	E/V
o-methylbenzophenone	2.22
o-methylacetophenone	2.31
5,8-dimethyl-α-tetralone	1.86
1,3,5-trimethoxybenzene	1.50
naphthalene	1.33

Scheme 1] followed by neutralization leads to re-formation of the starting material. In this mechanism incorporation of an isotopic tracer in the ketone takes place in the last step following neutralization. We believe that the reactions presented above take place at the semiconductor surface. If this were not the case, dissociation of the proposed radical-ion complex upon desorption giving a free radical should result in incorporation of deuterium into the methyl group of the ketone in the presence of an alcohol labelled in the alkyl group. This process based on hydrogen abstraction from the solvent molecules should reflect the difference in bond dissociation energy between C–H and O–H bonds.[15] Such a reaction was not observed in CD_3OH ruling out participation of free radicals in the reaction mechanism.

An alternative mechanism involving an exchange of the hydroxy hydrogen in enol radical cation is presented in Scheme 2. This mechanism seems to be less likely as compared to that presented in Scheme 1. Fast deprotonation of enol radical cations in alcohols[14] (Scheme 1) may effectively reduce their lifetime below limits expected for efficient exchange of hydrogens.[9,13]



Scheme 2

Acknowledgements

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