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BASE CATALYSED PHOTOCHEMICALLY INDUCED HYDROGEN ISOTOPE EXCHANGE IN *o*-METHYLBENZOPHENONE

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Photochemically induced hydrogen–deuterium and hydrogen–tritium exchange between *o*-methylbenzophenone and labelled methanol is shown to be catalysed by sodium carbonate. Both the (*E*) and (*Z*)-photoenols participate in the exchange reaction whereas in absence of the catalyst only the (*E*)-photoenol is reactive. Analysis of the measured quantum yields for hydrogen isotope exchange reaction allowed the determination of the relative population of transient photoenols and to its comparison with that obtained from the flash photolysis experiments. Both hydrogen kinetic and solvent isotope effects are discussed.

INTRODUCTION

Photoenolization of *o*-alkyl-substituted phenyl ketones has been extensively studied and the mechanism of this photoreaction is now well established.[1–7] Of the two transient photoenols, the (*Z*)-enol is very reactive and undergoes a rapid 1,5-sigmatropic hydrogen shift to regenerate the staring ketone. In contrast, the (*E*)-enol has a much longer lifetime and can participate in various chemical reactions. Even under cryogenic condition only the (*E*)-enol could be stabilized and it is believed that the (*Z*)-enol is formed under such conditions but reketonizes back, probably with an involvement of quantum-mechanical tunnelling.[8,9]

Hydrogen–deuterium[10,11] and recently also hydrogen– tritium[12] exchange have been applied to probe transient photoenol formation. These studies have shown that only (*E*)-enols participate in the exchange reaction. Addition of base as a catalyst is needed in order to induce the hydrogen exchange in the (*Z*)-enol.[11,13] It is expected that in this case the (*Z*)-enol is quenched by the base to form the enolate anion, which actually participates in the exchange process. A recent contribution by Scaiano *et al.*[14] provided a more systematic basis for understanding the effects of basis and acids on the quenching of (*E*)-photoenols. One may expect similar effects of bases and acids on the quenching of (*Z*)-photoenols.

This paper provides quantitative kinetic data for sodium carbonate-catalysed hydrogen–deuterium and hydrogen–tritium exchange in *o*-methylbenzophenone. These data are supplemented by laser flash photolysis measurements. Separation of both kinetic and solvent isotope effects allows one to differentiate the contributions of the two transient photoenols in the hydrogen isotope exchange reaction.

EXPERIMENTAL

Materials. *o*-Methylbenzophenone (MBP) (Aldrich) was used without further purification. Hydroxy-deuterated methanol (CH_3OD) (OPIDI, Poland; isotopic purity 99·5%) was used without further purification. Hydroxy-tritiated methanol (CH_3O^3H) (49·25 MBq mol^{-1}) was prepared by hydrogen–tritium exchange with tritium-labelled water (^3H_2O) (OPIDI) and was dried by a standard procedure.

Irradiation and product analysis. An argon-saturated solution of MBP (0·3 mol l^{-1}) and sodium carbonate (Na_2CO_3) in labelled methanol was irradiated ($\lambda = 300$ nm, $5{\cdot}45 \times 10^{16}$ quanta mol^{-1} s^{-1}) in a Rayonet merry-go-round photochemical reactor. After irradiation, the labelled ketone was separated from the reaction mixture by thin-layer chromatography (TLC). Incorporation of deuterium into the methyl group of MBP was analysed by mass spectrometry (Hewlett-Packard HP-5970 MSD mass spectrometer). The radioactivity of tritium-labelled MBP was measured with a liquid scintillation counter (LKB Wallac 1219 Rackbeta) using a solution of butyl-PBD (Koch-Light) (8 g l^{-1}) in dioxane as scintillator.

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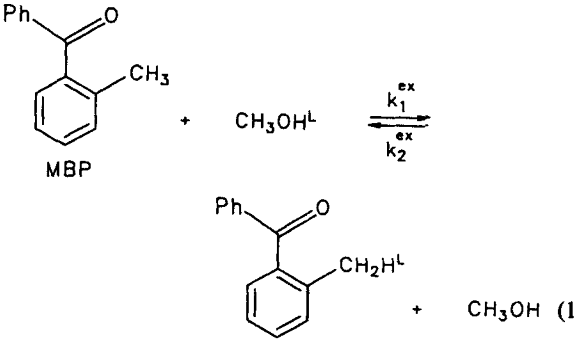
Calculation of quantum yields. In all experiments the irradiation time was as short as possible to secure a precise determination of labelled MBP. No side-products were observed. The amount of deuterium or tritium incorporated in MBP was always proportional to the irradiation time. Therefore, under the experimental conditions used, the reverse reaction [equation (1), k_2^{ex}] can be ignored. As reaction in the dark was not observed in the system studied, the quantum yield of the isotope exchange, Φ_{ex}, can be defined as the ratio of the number of ketone molecules exchanging hydrogen to the number of light photons absorbed in the solution.



(1)

H^L-deuterium or tritium

The quantum yields for hydrogen–deuterium exchange (Φ^{D}_{ex}) and hydrogen–tritium exchange (Φ^{T}_{ex}) were calculated from equations (2) and (3), respectively:

$$\Phi^{D}_{ex} = \frac{c_k N x}{It} \tag{2}$$

$$\Phi^{T}_{ex} = \frac{c_k N a_k}{a^{o}_{m} It} \tag{3}$$

where x = fractional population of deuterated molecules (fractions of CH_2D, CHD_2 and CD_3 were taken into account), a_k = molar tritium radioactivity of ketone, a^{o}_{m} = initial molar tritium radioactivity of methanol, c_k = molar concentration of ketone, N = Avogadro's number, I = light intensity and t = irradiation time. The values x/t in equation (2) and a_k/t in equation (3) were obtained from the slope of the linear relationship between amount of deuterium or tritium incorporated in MBP and the irradiation time. The error of the quantum yield determination estimated from the standard deviation of the slope determined by the least-squares method did not exceed 5%.

Laser flash photolysis. These studies were carried out in a 1 cm quartz cuvette employing the 355 nm third harmonic (pulse width 1 ns) from an Nd:YAG laser (NL100, Eksma) as excitation source. The output laser energy was about 20 mJ. The laser-induced transient absorption changes were monitored perpendicular to the excitation beam by the light from a Xenon arc lamp (Bausch and Lomb) focused and filtered with an interference filter (400 nm). The analysing light transmitted by the sample was monochromated with high resolution and detected with a Hamamatsu R 928 photomultiplier. The signal from the photomultiplier was recorded on a digitizing oscilloscope (Hewlett-Packard 54510A, 1GSa/s, two channels) and transferred via an interface (HP-IB) to an IBM AT computer where it was stored and analysed. The solutions were bubbled with helium and kept under a flux of gas. A detailed description of laser photolysis setup will be published elsewhere.[15]

RESULTS AND DISCUSSION

The quantum yields of photoinduced hydrogen–deuterium and hydrogen–tritium exchange between *o*-methylbenzophenone and the correspondingly labelled methanol in the presence and absence of sodium carbonate are given in Tables 1 and 2.

The deuterium-labelling experiments with *o*-methylbenzophenone confirmed the incorporation of deuterium into the *o*-methyl group only. As the tritium-

Table 1. Quantum yields of photoinduced hydrogen–deuterium exchange between *o*-methylbenzophenone and hydroxy-deuterated methanol in the absence and presence of sodium carbonate

$c_{Na_2CO_3}$ (10^{-4} mol l^{-1})	Φ^{D}_{ex}
0	0·085
0·95	0·160
1·56	0·173
3·04	0·185
4·57	0·198
8·52	0·231
9·43	0·243
11·90	0·250

Table 1. Quantum yields of photoinduced hydrogen–tritium exchange between *o*-methylbenzophenone and hydroxy-tritiated methanol in the absence and presence of sodium carbonate

$c_{Na_2CO_3}$ (10^{-4} mol l^{-1})	Φ^{D}_{ex}
0	0·019
0·90	0·046
1·43	0·052
3·00	0·060
4·72	0·073
8·50	0·080
11·00	0·081

and deuterium-labelling experiments were carried out under identical experimental conditions, the assumption that tritium labelling also occurs in the *o*-methyl group seems to be justified.

Based on previous studies of photochemically induced hydrogen isotope exchange,[10–12] we can safely assume that in the absence of sodium carbonate only the (*E*)-enol participates in the exchange reaction. The relatively long lifetime of the (*E*)-enol (of the order of seconds) is sufficient to achieve an equilibrium with labelled solvent. In contrast, the lifetime of the (*Z*)-enol is too short to exchange hydrogen with solvent.[11,12] Conclusive evidence is given later from analyses of lifetimes of the (*Z*)-enol of MBP measured in methanol and deuterated methanol.

Deuterium-labelling experiments were carried out in almost pure deuterated methanol (CH_3OD, isotopic purity 99·5%), in contrast to tritium labelling where the methanol used (CH_3OH) contained only traces of tritiated methanol. For that reason the quantum yields measured in deuterium-labelling experiments may include both primary kinetic and solvent isotope effects. For example, in order to separate kinetic and solvent isotope effects from the measured quantum yields of isotope exchange for the (*E*)-enol [$\Phi^{D}_{ex(E)} = 0{\cdot}085$ (Table 1) and $\Phi^{T}_{ex(E)} = 0{\cdot}019$ (Table 2)] we decided to study the dependence of the quantum yield for photoinduced hydrogen–deuterium exchange as a function of CH_3OD concentration in CH_3OH (Figure 1). The extrapolated value $\Phi^{D}_{ex(E)_0} = 0{\cdot}047$ to a concentration $c_{CH_3OD} \rightarrow 0$ allows one to separate deuterium–tritium primary kinetic isotope effect $\Phi^{D}_{ex(E)_0}/\Phi^{T}_{ex(E)_0} \approx 2{\cdot}5$ and the deuterium solvent isotope effect $\Phi^{D}_{ex(E)}/\Phi^{D}_{ex(E)_0} \approx 1{\cdot}8$. The value of the deuterium–tritium primary kinetic isotope effect of 2·5 is typical for room-temperature studies[16,17] and indicates that hydrogen atom transfer occurs as a rate-determining step in the exchange reaction studied. The solvent isotope effect value of 1·8 may indicate preferential formation of the (*E*)-enol in CH_3OD as compared with CH_3OH; in fact, this observation was confirmed by laser flash photolysis, and will be discussed later.

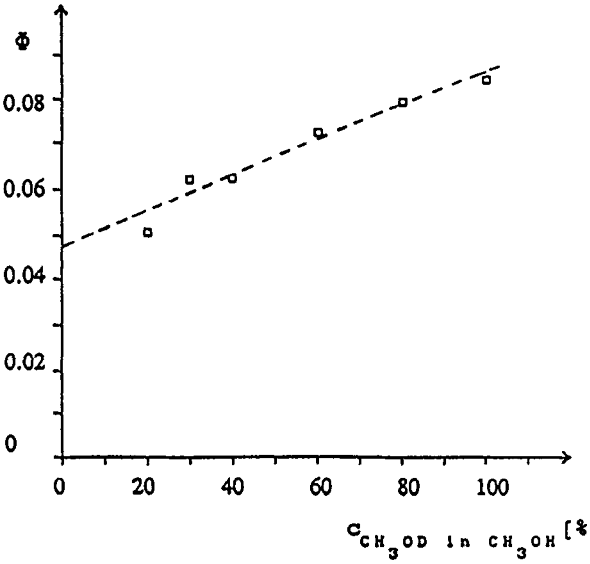
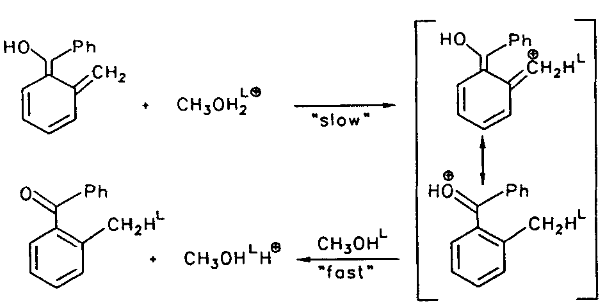


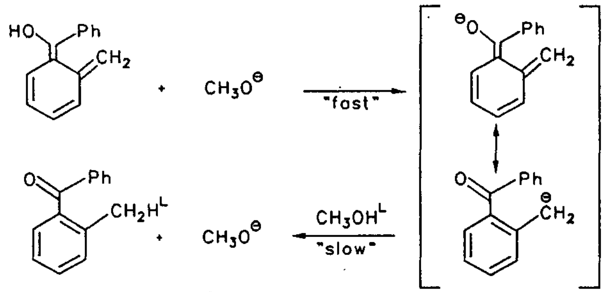
Figure 1. Quantum yield of hydrogen–deuterium exchange for the (*E*)-enol of *o*-methylbenzophenone as a function of CH_3OD concentration in CH_3OH

The exchange process in the (*E*)-enol can be initiated by free solvated $CH_3OH_2^+$ and CH_3O^- ions generated by autoprotolysis of methanol [reaction (4)][18] and proceeds according to the reaction sequence (5) or (6).

$$2\ CH_3OH^L \rightleftharpoons CH_3OH_2^{L\oplus} + CH_3O^{\ominus} \qquad (4)$$



(5)

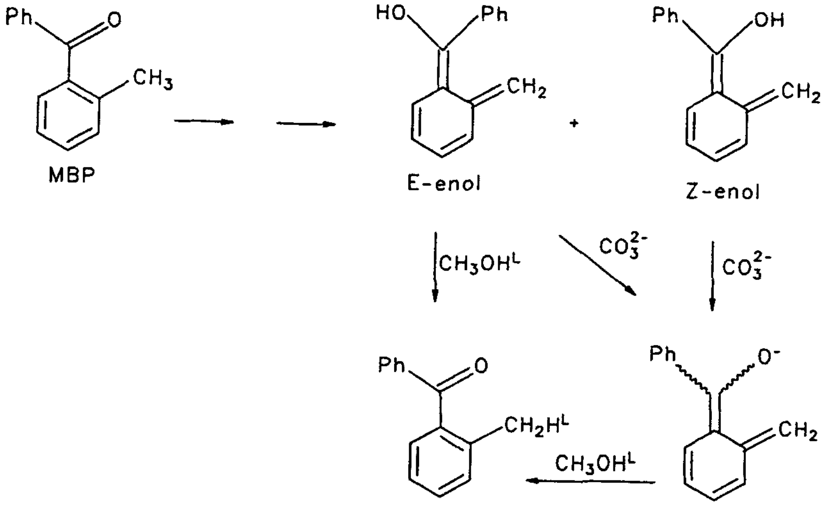


H^L-deuterium or tritium

(6)

The rate-determining step in the reaction sequence (5) or (6) is depicted as a 'slow' process and obeys proton transfer to a CH_2 group (between oxygen and carbon). In contrast, proton transfer from an enolic oxygen (between oxygen and oxygen) is considered to be a 'fast' process. Similar conclusions have been drawn from extensive studies on acid- or base-catalysed ketonization of enols carried out by Kresge's group.[19,20]

It is not surprising that the addition of sodium carbonate catalyses hydrogen exchange in the (*Z*)-photoenol, causing an increase in the observed quantum yield for the hydrogen isotope exchange.



H^L-deuterium or tritium

Scheme 1

Sodium carbonate can quench photoenols to form the corresponding enolate anions, which are expected to exchange hydrogens rapidly in hydroxylic solvents. All these possibilities are shown in Scheme 1.

This work, based on a quantitative approach, is aimed at the determination of rate constants for catalysed exchange reactions. Application of steady-state kinetics to the mechanism shown in Scheme 1 allows the derivation of the equation

$$\frac{1}{\Phi_{ex}-\Phi_{ex(E)}}=\frac{1}{\Phi_{ex(Z)}}+\frac{k_r}{k_b c_{Na_2CO_3}\Phi_{ex(E)}} \qquad (7)$$

where Φ_{ex} = observed quantum yield of the isotope exchange, $\Phi_{ex(E)}$ and $\Phi_{ex(Z)}$ = quantum yields of the isotope exchange for the (E) and (Z)-enol, respectively, k_r = unimolecular rate constant for reketonization of the (Z)-enol, k_b = bimolecular rate constant for sodium carbonate-catalysed hydrogen isotope exchange of the (Z)-enol and $c_{Na_2CO_3}$ = concentration of sodium carbonate. Linear plots of $1/\Phi_{ex}-\Phi_{ex(E)}$ against $1/c_{Na_2CO_3}$ for hydrogen–deuterium and hydrogen–tritium exchange are shown in Figure 2. From the intercept $\Phi_{ex(Z)}$ was found to be 0·159 (hydrogen–deuterium) and 0·074 (hydrogen–tritium). Assuming similar values of kinetic isotope effects for the Z and E isomers, one can easily determine the relative fraction of the (E)-enol in the enol mixture to be 34·8% (hydrogen–deuterium) and 20·4% (hydrogen–tritium).

Photoenol absorption decay curves in both CH_3OH and CH_3OD obtained in the laser flash photolysis experiments are presented in Figure 3. Assuming that the fast decay corresponds to the (Z)-enol and residual absorption which does not clearly decay on this time scale (slow decay) corresponds to the (E)-enol and that both enols have similar extinction coefficients, one may estimate the relative populations of the enols. It was found from these measurements that the relative population of the (E)-enol is 35·2% in CH_3OD and 22·1% in CH_3OH. These values correlate well with those obtained from the hydrogen isotope exchange experiments. The substantially higher relative population of the (E)-enol in CH_3OD may suggest that at the biradical stage, prior to spin inversion leading to enol formation, the equilibrium is shifted towards biradical retaining an *anti* conformation.[1–7] The relative energy of the hydrogen versus deuterium bonding interactions may play a crucial role in such equilibria.

The measured values of the (Z)-enol lifetimes of 4·48 μs ($k_r^H = 2{\cdot}23 \times 10^5\ s^{-1}$) in CH_3OH [Figure 3(A)] and 5·00 μs ($k_r^D = 2{\cdot}00 \times 10^5\ s^{-1}$) in CH_3OD [Figure 3(B)] indicate that the (Z)-enol does not participate seriously in the exchange of hydrogen for deuterium, otherwise the reketonization rate constant k_r^D should have been much lower than observed owing to the substantial kinetic isotope effect already evidenced for the (Z)-enol reketonization.[21,22] Assuming that $k_r^H \approx k_r^T$ and applying to equation (7) the data presented in Tables 1 and 2 as shown in Figure 2, one can calculate the rate constants for sodium carbonate-catalysed isotope exchange of the (Z)-enol, which were found to be $k_b^D = 1{\cdot}72 \times 10^9\ l\,mol^{-1}\,s^{-1}$ and $k_b^T = 1{\cdot}45 \times 10^9\ l\,mol^{-1}\,s^{-1}$. Since enolate anions participate in the base-catalysed hydrogen isotope exchange, the found values of k_b should, in principle, be comparable to the rate constants for the quenching of the (Z)-enol by sodium carbonate. Such values are not available in the literature.

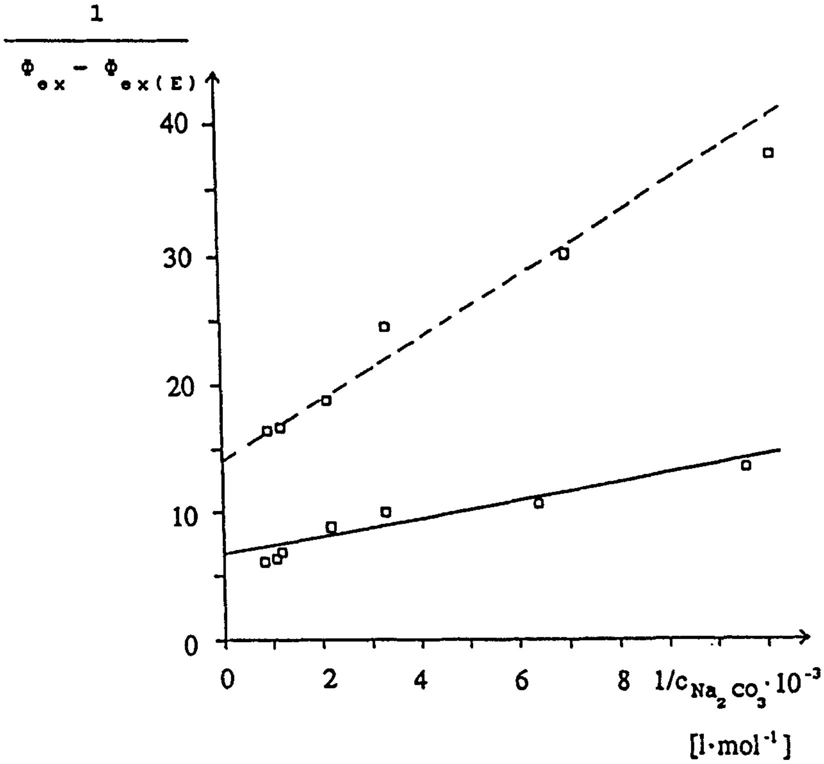


Figure 2. Dependence of $1/\Phi_{ex} - \Phi_{ex(E)}$ on $1/c_{Na_2CO_3}$ for hydrogen–deuterium (solid line) and hydrogen–tritium (dashed line) exchange in *o*-methylbenzophenone

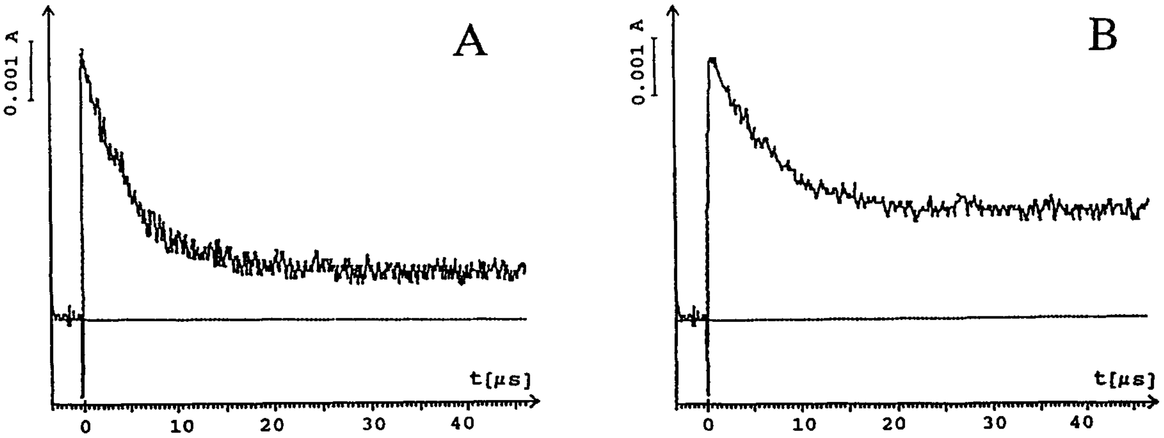


Figure 3. Absorption decay curves for transient photoenols of *o*-methylbenzophenone monitored by laser flash photolysis at 400 nm in deoxygenated CH_3OH (A) and CH_3OD (B)

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