# PROBING OF TRANSIENT PHOTOENOL FORMATION FROM ORTHO-METHYL-SUBSTITUTED PHENYL KETONES BY HYDROGEN–TRITIUM EXCHANGE

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**Studies on the photochemically induced hydrogen–tritium exchange in *o*-methyl-substituted phenyl ketones are reported. It is shown that the tritium exchange can be beneficial for probing transient photoenol formation, particularly when photochemical side-reactions are occurring.**

The photochemistry of *o*-methyl-substituted phenyl ketones has been extensively studied and a number of comprehensive reviews have been published.[1–4] The evidence for transient photoenol formation is substantial and includes UV, visible and IR absorption spectra,[5,6] deuterium exchange,[7] oxygenation[8–10] and trapping experiments with dienophiles.[11–14]
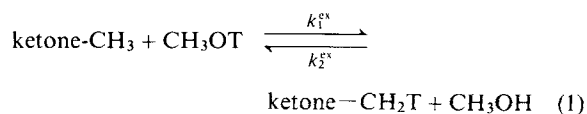
Studies of the hydrogen–deuterium exchange were aimed at the preparation of deuterium-labelled compounds to obtain evidence for the presence of transient photoenols. Such efforts were often unsuccessful owing to the occurrence of photochemical side-reactions leading to substantial consumption of the reacting material. Quantum yields of isotope exchange reactions have not yet been measured.

In this paper we report studies on the photochemically induced hydrogen–tritium exchange in *o*-methyl-substituted phenyl ketones. The use of tritium instead of deuterium provided an opportunity to monitor the isotope exchange reaction after short irradiation times. On the other hand, quantum yields of isotope exchange reactions can be evaluated with fairly high precision. In spite of the difficulties concerning the monitoring of positional reactivities without chemical degradation of the reacting molecules, it seems that the application of tritium labelling is beneficial.

Deoxygenated solutions of ketones (0·3 M) in methanol labelled with tritium in the hydroxy group (0·5 GBq mol$^{-1}$) were irradiated in a Rayonet merry-go-round photochemical reactor equipped with eight lamps emitting at 300 nm (1·2 × 10$^{18}$ quanta ml$^{-1}$ min$^{-1}$). After irradiation, the ketones were separated by thin-layer chromatography (TLC) and their radioactivities were measured by liquid scintillation counting. Using the same experimental conditions, test experiments were run in methanol labelled with deuterium in the hydroxy group (isotopic purity 99·5%) and positional reactivity was monitored by mass spectrometry.

The radioactivity of tritium incorporated in a ketone was always proportional to the irradiation time. Short irradiation times (15–120 min) did not allow for the formation of noticeable amounts of side-products. Further, the reverse [equation (1)]

$$\text{ketone-CH}_3 + \text{CH}_3\text{OT} \underset{k_2^{ex}}{\overset{k_1^{ex}}{\rightleftharpoons}} \text{ketone-CH}_2\text{T} + \text{CH}_3\text{OH} \quad (1)$$

($k_2^{ex}$) leading to a transfer of tritium (T) from labelled ketones to methanol can be ignored under the experimental conditions used. As reaction in the dark has not been observed in the system studied, the quantum yield of the isotope exchange, $\Phi_{ex}^T$, can be defined as a ratio of the number of ketone molecules exchanging hydrogen to the number of light photons absorbed in the solution. This definition leads to equation (2), which was applied for the calculation of $\Phi_{ex}^T$.

$$\Phi_{ex}^T = \frac{c_k N a_k}{a_m^0 I t} \quad (2)$$

where $a_k$ = molar tritium radioactivity of ketone, $a_m^0$ = initial molar tritium radioactivity of methanol, $c_k$ = molar concentration of ketone, $N$ = Avogadro's number, $I$ = light intensity and $t$ = irradiation time.

The value of $a_k/t$ was obtained from the slope of the linear relationship between the specific radioactivity, $a_k$, incorporated in the ketone and the irradiation time. All other values in equation (2) were constant. 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%.

The values of the quantum yields of the hydrogen–tritium exchange are summarized in Table 1. Introducing a methyl substituent in the *ortho* position of **1** substantially increased $\Phi_{ex}^T$. In **1** the exchange reaction involved the ring hydrogens and the value of $\Phi_{ex}^T$ obtained is typical.[15] As was stated before,[7] the deuterium labelling in **2** proceeded via a transient photoenol and the deuterium was incorporated into the *o*-methyl group. Our deuterium labelling experiments on **2** confirmed the incorporation of deuterium into the *o*-methyl group only. As our tritium 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. Labelling experiments with the model ketone **1** without an *o*-methyl substituent support this view.

In principle, the two enols can participate in the exchange, i.e. the short-lived (*Z*)-enol or the long-lived (*E*)-enol.[5] In order to verify which photoenol participates in the isotope exchange, we used 5,8-dimethyl-1-tetralone (**4**), which can only form the enol in a *Z*-configuration. We could not detect any substantial exchange in **4** and we conclude that the (*Z*)-enols are too short-lived to exchange hydrogen for
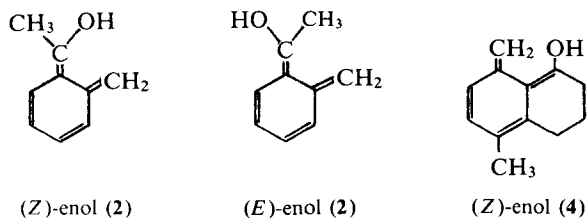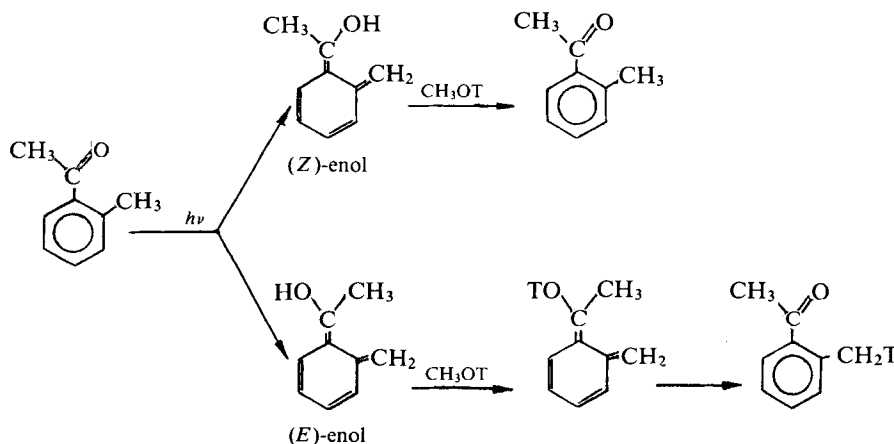
Table 1. Quantum yields of photoinduced hydrogen–tritium exchange between *o*-methyl-substituted phenyl ketone and tritium-labelled methanol

| Ketone | Structure | $10^2\Phi_{ex}^T$ |
|---|---|---|
| Acetophenone (**1**) | | 0·09 |
| 2-Methylacetophenone (**2**) | | 6·03 |
| 2,4,6-Trimethylacetophenone (**3**) | | 2·30 |
| 5,8-Dimethyl-1-tetralone (**4**) | | 0·20 |

(*Z*)-enol (**2**)          (*E*)-enol (**2**)          (*Z*)-enol (**4**)

Scheme 1

tritium. A similar conclusion has been already drawn from the deuterium labelling experiments.[5] The value of $\Phi_{ex}^T$ for **2** (6·03%) is smaller than $\Phi_{ex}^D$ estimated for deuterium labelling (15%). Both $\Phi_{ex}^D$ and $\Phi_{ex}^T$ are lower than the total triplet yield (52%),[16] indicating that only a fraction of the enol exchanges hydrogen for deuterium or tritium. The value of $\Phi_{ex}^D/\Phi_{ex}^T \approx 2\cdot5$ may include both kinetic and solvent isotope effects. Further experiments are needed to find the value of the primary kinetic isotope effect. The mechanism proposed is shown in the Scheme 1.

Deuterium labelling experiments with **3** have not been fully explained.[1,17,18] Efficient formation of benzo-cyclobutenol (**5**) was observed in that case. It was suggested that the exchange could occur at the benzo-cyclobutenol stage, followed by a photosensitized ring opening reaction to give the triplet diradical, which collapses back to the starting ketone. An alternative explanation might involve participation of the (E)-enol despite the fact that the ground-state enol has not been trapped by dienophiles.[1,19] Our experiments seem to clarify this matter. We have detected hydrogen–tritium exchange under experimental conditions where the formation of **5** was practically zero (not seen on the TLC plate). Hence the route involving secondary photochemistry to form a labelled ketone is very unlikely. The hydrogen–tritium exchange in the case of **3** took place at the photoenol stage and it was not surprising that the quantum yield was lower than that with **2**, simply because a non-planar ground-state conformation did not favour a photoenolization process.
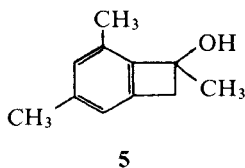
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REFERENCES

1. P. G. Sammes, *Tetrahedron* **32**, 405–422 (1976).
2. P. J. Wagner, in *Rearrangements in Ground and Excited States*, P. de Mayo, (ed.), Vol. 3, pp. 381–443. Academic Press, New York (1980).
3. J. C. Scaiano, *Acc. Chem. Res.* **15**, 252–258 (1982).
4. P. J. Wagner, *Acc. Chem. Res.* **16**, 461–467 (1983).
5. R. Haag, J. Wirz and P. J. Wagner, *Helv. Chim. Acta* **60**, 2595–2607 (1977).
6. J. Gębicki and A. Krantz, *J. Chem. Soc., Perkin Trans. 2* 1623–1627 (1984).
7. G. Wettermark, *Photochem. Photobiol.* **4**, 621–622 (1965).
8. P. Yates, A. C. Mackay and F. X. Garneau, *Tetrahedron Lett.* 5389–5392 (1968).
9. M. Pfau, E. W. Sarver and N. D. Heindel, *Bull. Soc. Chim. Fr.* 183–189 (1973).
10. B. J. Arnold, P. G. Sammes and T. W. Wallace, *J. Chem. Soc., Perkin Trans. 1* 415–420 (1974).
11. F. Nerdel and W. Brodowski, *Chem. Ber.* **101**, 1398–1406 (1968).
12. M. Pfau, N. D. Heindel and T. F. Lemke, *C. R. Acad. Sci.* **261**, 1017–1018 (1965).
13. N. D. Heindel, E. W. Sarver and M. Pfau, *Tetrahedron Lett.* 3579–3582 (1968).
14. B. J. Arnold, S. M. Mellows, P. G. Sammes and T. W. Wallace, *J. Chem. Soc., Perkin Trans. 1* 401–409 (1974).
15. W. J. Spillane, in *Isotopes in Organic Chemistry, Vol. 4, Tritium in Organic Chemistry*, E. Buncel and C. C. Lee, (eds), pp. 51–84, Elsevier, Amsterdam (1978).
16. P. J. Wagner, *Pure Appl. Chem.* **49**, 259–270 (1977).
17. T. Matsuura and Y. Kitaura, *Tetrahedron Lett.* 3309–3310 (1967).
18. T. Matsuura and Y. Kitaura, *Tetrahedron* **25**, 4487–4499 (1969).
19. H. Lutz, E. Breheret and L. Lindqvist, *J. Chem. Soc., Faraday Trans. 1* **69**, 2096–2102 (1973).