

INVESTIGATIONS INTO A POSSIBLE ^{14}C ISOTOPE EFFECT IN PHOTODISSOCIATIONS

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Abstract—The photo-Fries rearrangement of *p*-methoxyphenylacetate-carboxyl- ^{14}C and the photo-decarboxylation of *p*-nitrophenylacetic acid-carboxyl- ^{14}C were investigated in order to evaluate a possible ^{14}C isotope effect. In both cases k_{12}/k_{14} is found to be unity within experimental error.

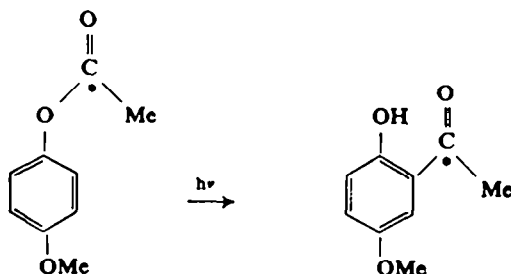
This is in agreement with the conception that in many photochemical processes in solution the reaction—starting from the electronically excited state—occurs as a kind of internal conversion to the ground state of the primary product. There is no activation energy needed in the sense encountered in thermal reactions.

INTRODUCTION

THE question has been raised whether photochemical reactions after electron excitation pass through a transition state of appreciable energy of activation. In the present study the ^{14}C isotope effect was investigated in two primary photodissociations since in these the first reaction step after excitation involves the rupture of a bond. As competing processes such as fluorescence, internal conversion, quenching and inter-system crossing may be independent of the isotope, a possible difference in the rate of bond breaking would be expected to appear in the reaction rate. The magnitude of such an isotope effect may give information about the reaction path followed in the primary photodissociation.

A. Photo-Fries reaction of *p*-methoxyphenylacetate-carboxyl- ^{14}C

This reaction has been extensively investigated in this laboratory by Stratenus.¹ The dissociation of the ester C—O bond seems to take place starting from the first singlet excited state.



EXPERIMENTAL

Labelled *p*-methoxyphenylacetate was prepared from *p*-methoxyphenol and Ac_2O which had been refluxed with $\text{AcONa-1-}^{14}\text{C}$ (Radiochemical Centre, Amersham); m.p. 31–32°. (Found: C, 65.4; H, 6.2. Calc. for $\text{C}_9\text{H}_{10}\text{O}_3$: C, 65.1; H, 6.0%.) The specific radioactivity: $a_s = 0.387 \mu\text{Ci/mmole} \pm 1.5\%$.

¹ J. L. Stratenus, Thesis, Leiden (1966).

A soln of ^{14}C -*p*-methoxyphenylacetate (500 mg) in alcohol (800 ml) was illuminated with a Hanau Q 81 UV lamp (CuSO_4 filter). The progress of the reaction was estimated spectrophotometrically, assuming that the rearrangement product, 2-aceto-4-methoxyphenol, and the byproduct, *p*-methoxyphenol, are formed in the ratio 1:2:1.¹ The solvent was evaporated and the residue was steam distilled. The distillate was extracted with ether. The ether layer was washed with 0.1N NaOH. From this layer the starting product was isolated and recrystallized from toluene-ligroin.

The NaOH layer was acidified and extracted with ether. From the ether layer the product, 2-aceto-4-methoxyphenol, was isolated and recrystallized from MeOH; m.p. 46° . (Found: C, 64.5; H, 5.9. Calc. for $\text{C}_9\text{H}_{10}\text{O}_3$: C, 65.1; H, 6.0%.)

The specific radioactivities were determined by weighing accurately about 1 mg of the compound and counting this sample in a toluene-PPO (5 g/l.)-dimethyl-POPOP (0.3 g/l.) mixture by means of a liquid scintillation counter (I.D.L. 2022, 2032). ^{14}C -toluene was used as an internal standard. This procedure was repeated ten times, thus reducing the error to less than 2%.

RESULTS

The isotope effect was computed from the specific activities of the original *p*-methoxyphenylacetate ($a_o = 0.387 \mu\text{Ci}/\text{mmole}$) and of the product (a_i) or of the remaining reactant (a_r):

$$\frac{a_o}{a_i} = \frac{1}{f} \left(1 - (1 - f)^{k_{13}/k_{14}} \right); \quad \frac{a_i}{a_o} = (1 - f)^{k_{13}/k_{14} - 1}$$

f is the extent of the reaction.²

Table 1 shows that, within the experimental error of 2%, the photo-Fries reaction

TABLE 1. DETERMINATION OF ^{14}C ISOTOPE EFFECT IN THE PHOTO-FRIES REACTION OF *p*-METHOXYPHENYLACETATE FORMING 2-ACETO-4-METHOXY-PHENOL

Run	f	a_i	a_r	k_{13}/k_{14}
1	0.55	—	0.387	1.00
2	0.30	—	0.383	1.01 ^a
3	0.69	0.391	0.391	1.01 ^a 0.98
4	0.44	0.383	0.381	0.97 ^a 1.02
5	0.50	0.393	0.380	1.02 1.03

$a_o = 0.387 \mu\text{Ci}/\text{mmole}$

Average: $k_{13}/k_{14} = 1.007 \pm 0.018$

studied exhibits no isotope effect. From the C—O stretching frequency (1205 cm^{-1})³ the maximum isotope effect for bond rupture in the ground state may be computed⁴ to be about 1.13. From calculations of the bond orders of the ground state and of the lowest singlet excited state a considerable difference in C—O bond strength is not to

¹ C. J. Collins in *Advances in Physical Organic Chemistry* (Edited by V. Gold). Vol. II; p. 74. Academic Press, London and New York (1964).

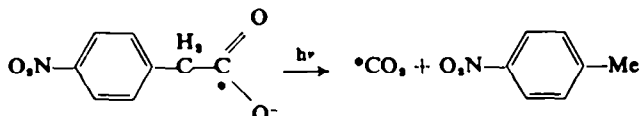
² G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. II, p. 195. D. van Nostrand Company, Inc., Princeton, N.J. (1945).

³ L. Melander, *Isotope Effects on Reaction Rates*, p. 17. The Ronald Press Comp., New York (1960).

be expected;⁵ for the photodissociation a maximum isotope effect of ~ 1.13 seems a reasonable guess.

B. Photodecarboxylation of *p*-nitrophenylacetic acid-carboxyl- ^{14}C

The formation of CO_2 in the photodecarboxylation of *p*-nitrophenylacetic acid⁶ evidently takes place in a single step after the photoexcitation. The magnitude of a kinetic isotope effect should yield information on the nature of this reaction step.



EXPERIMENTAL

p-Nitrophenylacetic acid was prepared from benzylchloride and $\text{Na } ^{14}\text{CN}$ (Radiochemical Centre, Amersham); m.p. $151\text{--}152^\circ$.⁷

A soln of *p*-nitrophenylacetic acid- ^{14}C (90 mg) in 0.1N Ba(OH)_2 (100 ml) in a pyrex Erlenmeyer flask was illuminated by a Philips HP 125 W UV lamp (typ. 57202 E) in a glove box to prevent CO_2 exchange with the air. At set intervals the solution was filtered through a Schleicher and Schüll 1575 filter paper. The filter paper with the BaCO_3 formed was treated with conc H_2SO_4 .⁸ The CO_2 evolved was trapped in a liquid scintillation soln consisting of toluene-methyl cellosolve-ethanolamine (10:8:1) and PPO (5 g/l.). The amount of CO_2 was determined by titration with a 0.025M MeONa soln in toluene-MeOH (10:1) using phenolphthalein as an indicator. After titration the soln was counted in the same vessel in a liquid scintillation counter (I.D.L.). As an internal standard ^{14}C -toluene was employed.

The specific activity of the *p*-nitrophenylacetic acid- ^{14}C was determined by dissolving a few crystals in the scintillation soln. Titration and counting were performed as in the $^{14}\text{CO}_2$ determinations. Averaging 10 determinations the specific activity was found to be: $a_s = 1.57 \pm 0.06 \mu\text{Ci/mmole}$.

RESULTS

The isotope effect of the photodecarboxylation of *p*-nitrophenylacetic acid was determined using the differential method.³ The specific activity of the CO_2 formed was plotted against the amount of CO_2 titrated (Fig. 1).

The specific activity proved to be constant and equal to the initial a_s up to 3 hr of illumination or at least 55% conversion. The values then decreased. This could be due to the formation of CO_2 from other atoms by overirradiation or to the uptake of atmospheric CO_2 . If an isotope effect should occur, the values would be expected to increase. For a dissociation in the ground state a maximum isotope effect of about 1.09 may be computed⁴ from the C—C stretching frequency (900 cm^{-1})³.

CONCLUDING REMARKS

In the terminology of the transition state theory the absence of an isotope effect might be interpreted as indicating that the dissociating bond is still largely intact in the transition state.

⁴ W. Th. A. M. van der Lugt, Personal communication.

⁵ J. D. Margerum, as quoted in J. G. Calvert, J. N. Pitts jr., Photochemistry, p. 433. John Wiley and Sons, London (1966).

⁶ A. I. Vogel, Practical Organic Chemistry, p. 763. Longmans, Green and Co., London.

⁷ A. Patchornik, Y. Shaltin, Anal. Chem. 33, 1887 (1961).

A more simple conception in agreement with the experimental findings consists of a reaction path that starts from the electronically excited state of the reactant and cascades down via a series of vibrationally excited states towards the ground state of the product. This process, which may be considered as a kind of internal conversion, requires no thermal energy of activation. Once the down hill process has started in solution it will be finished in a very short time (10^{-11} sec).

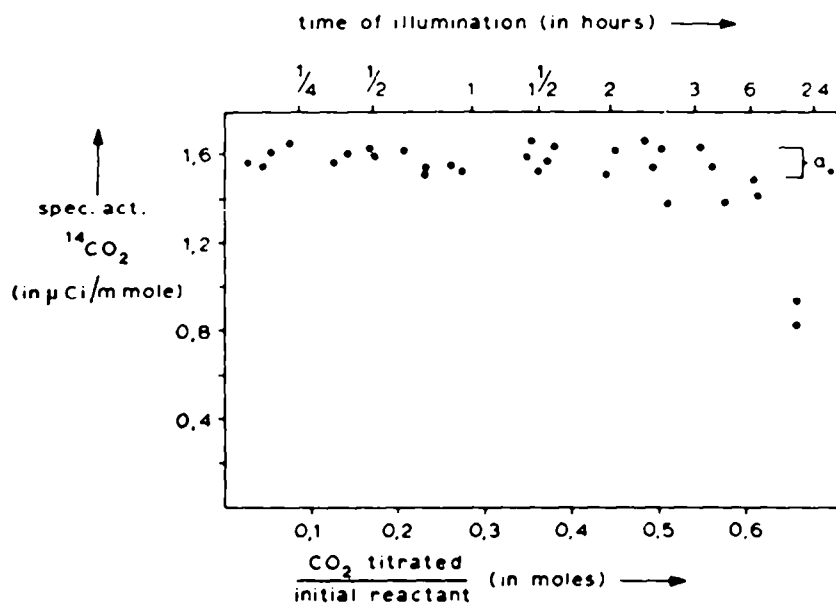


FIG. 1. Determination of the isotope effect in the photodecarboxylation of *p*-nitrophenylacetic acid using the differential method (5 reaction runs).

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