Short Communication

The reaction of 2-pentanone triplets with carbon tetrachloride

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(Received March 15, 1974)

Carbon tetrachloride is a potentially useful solvent for photochemical studies but its reactivity towards excited ketones is uncertain. For instance, it has been recently reported that most or the effect of carbon tetrachloride in benzophenone photochemistry is due to impurities. When these are removed, the triplet lifetime is only sligthly shorter than in inert solvents, probably owing to a heavy atom effect [1]. On the other hand, there is strong evidence that the excited singlet state of aliphatic ketones is quenched by the following reaction [2] :

$$^1K + CCl_4 \rightarrow K + Cl_3C^{\cdot} + Cl^{\cdot} \tag{1}$$

In the present work, we present evidence showing that acetone and 2-pentanone triplets also react in a similar way.

The photolyses were carried out in a "merry-go-round" apparatus at 25 °C and in n-hexane solution. Since a medium pressure mercury lamp was employed and the reaction tubes were made of Pyrex, most of the absorbed radiation was in the 3130 Å region. Acetone and 2-pentanone concentrations were lower than 0.2 M.

Acetone and chloroform were analyzed by gas chromatography. 2-Pentanone was employed as actinometer. It was assumed that the acetone quantum yield is 0.3 [3].

The results obtained were found to be independent of conversion and the carbon tetrachloride employed (Hopkins & Williams, general purpose reagent; Carlo Erba; U.C.B., Bruxelles; Merck, pro-analyses; Merck, spectrograde, 99.7% pure; Merck, spectrograde, photobrominated and distilled).

The photolysis of acetone in the presence of carbon tetrachloride gave hydrochloric acid and chloroform as products even at carbon tetrachloride concentrations which render singlet quenching negligible [2]. For example, with a carbon tetrachloride concentration of 0.033 M we obtained:

$$\Phi_{HCl} = 0.40 \pm 0.10$$

and

$$\Phi_{CHCl_3} = 0.38 \pm 0.05$$

where the error involved in the HCl determination is rather high owing to the method employed (pouring of the photolyzed solution in water and pH determination). At higher carbon tetrachloride concentrations the HCl quantum yields tend towards 1 but the $CHCl_3$ quantum yield decreases probably due to $Cl_3C^{\bullet}$ combination.

Kinetic results were obtained for the quenching of 2-pentanone triplets. A plot of:
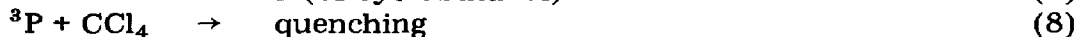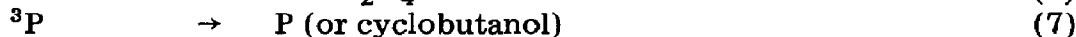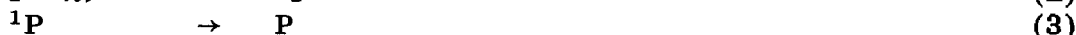
$$[\Phi_A^0 - (\Phi_A^0)_s] \, / \, [\Phi_A - (\Phi_A^0)_s]$$

where

Φ_A^0 = acetone quantum yield without added carbon tetrachloride; and

$(\Phi_A^0)_s$ = acetone quantum yield from the singlet state without added carbon tetrachloride (obtained in the presence of 0.3 M 1,3-pentadiene [3, 4]) against carbon tetrachloride concentration was linear in the 0 to 0.5 M concentration range. At higher concentrations an upward curvature appears probably owing to the quenching of the singlet state [2].

The results obtained at low carbon tetrachloride concentrations are compatible with a simple mechanism comprising reactions (2) to (8):

$P + h\nu$	$\rightarrow$	^1P	(2)
^1P	$\rightarrow$	P	(3)
^1P	$\rightarrow$	$A + C_2H_4$	(4)
^1P	$\rightarrow$	^3P	(5)
^3P	$\rightarrow$	$A + C_2H_4$	(6)
^3P	$\rightarrow$	P (or cyclobutanol)	(7)
$^3P + CCl_4$	$\rightarrow$	quenching	(8)

From the slope of the plot it was found that $k_8\tau_T = 3.0 \ M^{-1}$, where τ_T is the triplet lifetime in the n-hexane solvent. Taking $\tau_T = 2.5 \times 10^{-7}$ s [5] we obtain $k_8 = 1.2 \times 10^7 \ M^{-1} \ s^{-1}$.

If the quenching reaction is represented by:

$$^3P + CCl_4 \rightarrow P + Cl_3C^{\bullet} + Cl^{\bullet} \qquad (9)$$

and assuming that all the chlorine atoms lead to HCl, eqn. (10) should hold:

$$[A]^0 - [A] = a \, [HCl] \qquad (10)$$

where

$[A]^0$ = concentration of acetone obtained without added carbon tetrachloride, and

a = fraction of 2-pentanone triplets leading to acetone and ethylene. In a typical run (carbon tetrachloride concentration 0.26 M) we have found that $[A]^0 - [A] = 0.3 \times 10^{-2} \ M$ and $(HCl) = 1.3 \times 10^{-2} \ M$. Since $a = 0.34$ [5], both results are of the expected order if we take into account the high error involved in the HCl determination.

The possibility of significant triplet quenching by impurities can be

disregarded since: (a) the values of $k_8\tau_T$ are independent of the carbon tetrachloride source; (b) the carbon tetrachloride concentration for half quenching is nearly $0.35\ M$. The maximum impurity concentration is, at this carbon tetrachloride concentration, nearly $10^{-3}\ M$ (assuming 0.3% of impurity and a similar molecular weight. To explain our results, all the impurity would have to be a "diffusional quencher"; (c) the impurity active in benzophenone quenching was a chlorinated olefin. This type of compound is not expected to behave as a diffusional quencher for an aliphatic ketone; (d) the extent of quenching was not modified by photobromination of the carbon tetrachloride. This treatment should reduce the amount of reactive olefins; (e) hydrochloric acid and chloroform are produced in amounts compatible with reaction (9).

The mechanism for the energy transfer that leads to reaction (9) can be considered as similar to that discussed for the singlet quenching [2]. The value found for reaction (9) in the present work is nearly ten times smaller than that reported for the quenching of 3-pentanone singlets. This difference can be probably related to the higher exothermicity of the singlet reaction.

1   D. Schuster and T. M. Weil, Mol. Photochem., 4 (1972) 447.
2   J. O. Pavlik, P. I. Plocard, A. C. Somersall and J. E. Guillet, Can. J. Chem., 51 (1973) 1435.
3   P. J. Wagner and G. S. Hammond, J. Am. Chem. Soc., 88 (1966) 1245.
4   F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro and J. C. Dalton, J. Am. Chem. Soc., 92 (1970) 1793.
5   E. B. Abuin, M. V. Encina and E. A. Lissi, J. Photochem., in press.