The Reaction of Diphenylmethylene with Isopropyl Alcohol and Oxygen: the Question of Reversibility of Singlet–Triplet Interconversion of Carbenes

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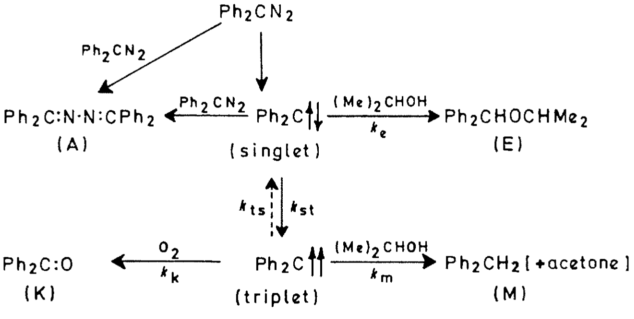
Summary The dependence on added isopropyl alcohol concentration of the proportions of products formed by thermal decomposition of the diphenyldiazomethane in acetonitrile is consistent with reversible interconversion of the singlet and triplet states of the intermediate diphenylmethylene.

TRANSFORMATION of initially-formed singlet carbenes into their triplet states has provided a plausible interpretation of the products formed in a number of reactions.[1] Some time ago[2] we tentatively suggested that in the case of diphenylmethylene in aromatic hydrocarbon solvents, the interconversion of singlet and triplet states might be reversible. Similar suggestions have been made by others[3] with reference to other carbenes, but unambiguous evidence has so far been lacking. We report here preliminary results from a more detailed investigation of spin inversion in diphenylmethylene.



SCHEME

Thermal decomposition at 85° of diphenyldiazomethane (*ca.* 0·05 M) in acetonitrile containing isopropyl alcohol (0·5—2·5 M) produces benzophenone azine (A), diphenylmethyl isopropyl ether (E), and diphenylmethane (M). When oxygen is present, benzophenone (K) is also formed,

TABLE 1

Product yields[a] *for thermal decomposition of diphenyldiazomethane at* 85°[b] *in oxygen-saturated acetonitrile containing isopropyl alcohol*

		Products (%)[a]					
[Pr^{i}OH] (M)	*n*[c]	E	M	K	A	10^2 M/E	10^2 M/K
0·50	6	34·5	2·0	45·2	17·3	5·9	4·6
1·00	3	51·7	3·3	29·8	14·2	6·4	11·2
1·50	6	53·2	3·8	25·7	16·5	7·1	14·9
2·00	3	59·2	4·3	22·3	13·2	7·2	19·2
2·50	6	59·8	4·6	19·2	15·5	7·7	24·0

[a] Average % Ph_2CN_2 converted into each product. A was determined by u.v. spectroscopy. E, M, and K were obtained by g.l.c. (2 m x 5 mm copper column with 1·25% Carbowax 20 M + 3·75% S.E. 30 supported on 60/80 mesh silanised G-Cel celite at 180°).

[b] The temperature of the thermostatically controlled bath containing the reaction vessels. The temperature of the reaction solutions was slightly less than this, the difference increasing with increasing [Pr^{i}OH].

[c] Number of separate analyses.

but the amount can be reduced (though not completely eliminated[4]) by standard deoxygenation procedures. Table 1 contains average values (accurate to ±5% of the recorded figure) of the yields of these products for reactions carried out in open glass vessels into which oxygen, saturated with the solvent, was passed. The oxygen concentration in the reaction mixtures, as indicated by a Rank oxygen electrode, did not vary with changing isopropyl alcohol concentration. Table 2 contains product analyses for reactions carried out under nitrogen in sealed polytetrafluoroethylene vessels which had been deoxygenated by standard procedures. Though not insignificant, the oxygen concentration in these solutions is small and probably fairly constant.

TABLE 2

Product yields for thermal decomposition under nitrogen of diphenyldiazomethane at 85° *in acetonitrile containing isopropyl alcohol*

		Products (%)[a]				
[Pr^{i}OH] (M)	*n*	E	M	K	A	10^2 M/E
0·61	8	57·1	4·3	3·0	34·6	7·5
0·99	4	77·6	5·9	0·9	14·6	7·6
1·48	5	77·1	5·7	2·4	13·8	7·4
2·01	8	76·6	5·9	2·0	14·5	7·7

[a] See footnote a to Table 1. The g.l.c. analysis used a 2m × 5mm glass column with 1% O.V. 17 supported on Gaschrom Q at 120°.

The rough constancy of the ratio M/E with changing concentration of isopropyl alcohol, [Pr^{i}OH], (Tables 1 and 2) and the proportionality of M/K to [Pr^{i}OH] are consistent with a reaction scheme in which isopropyl alcohol and oxygen compete for a single intermediate carbene yielding E + M and K, respectively. However, it is more plausible to regard M and K as the products of reaction of triplet diphenylmethylene with the alcohol and oxygen, respectively, with E and part of the azine derived by attack of the singlet carbene on isopropyl alcohol and unchanged diazoalkane.† Such a reaction sequence is shown in the Scheme.

A conventional steady-state kinetic treatment leads to expression (1). If reversion of triplet diphenylmethylene

$$\frac{d(M + K)}{dE} = \frac{k_{st}(k_m[Pr^iOH] + k_k[O_2]}{k_e[Pr^iOH](k_m[Pr^iOH] + k_k[O_2] + k_{ts})} \qquad (1)$$

to the singlet state does not compete with formation of M and K, *i.e.* $k_{ts} = 0$, then $(M + K)/E = k_{st}/k_e\,[Pr^iOH]$. The opposite limiting situation, found when $k_{ts} \gg k_m [Pr^iOH] + k_k [O_2]$, is given by equation (2). Under our

$$\frac{M + K}{E} = \frac{k_{st}}{k_e k_{ts}}\left(k_m + \frac{k_k\,[O_2]}{[Pr^iOH]}\right) \qquad (2)$$

reaction conditions, (M + K)/E should be a linear function of $[Pr^iOH]^{-1}$ and triplet to singlet conversion should be evidenced by a non-zero intercept.

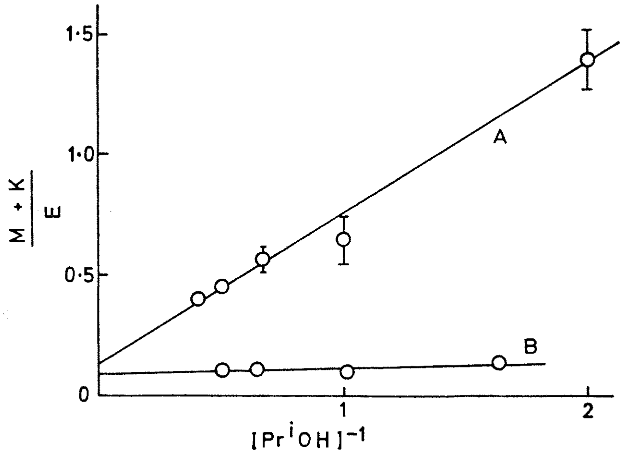


FIGURE. *Test of equation* (2) *using data summarised in Tables* 1 (*line* A) *and* 2 (*line* B). *The lines drawn were calculated by linear regression analysis and the intercepts are* 0·13 ± 0·03 (*line* A) *and* 0·086 ± 0·019 (*line* B).

Graphs of (M + K)/E against $[Pr^iOH]^{-1}$ using the data of Tables 1 and 2 are shown in the Figure. It is evident that the intercept at $[Pr^iOH]^{-1} = 0$ is not zero and is the same within the experimental uncertainty for reactions under the two sets of conditions. Thus the present results, while consistent with a single carbene precursor of E, M, and K, are also consistent with participation by both singlet and triplet states of diphenylmethylene, but only if these states equilibrate freely. The reversibility of interconversion of singlet and triplet states of carbenes has important

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† Part of the azine is formed by a reaction between two diazoalkane molecules, probably on a surface, without intermediate formation of diphenylmethylene.[5]

implications in relation to discussions of carbene reactivity and the stereochemistry of carbene reactions.

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See, for example, W. Kirmse, "Carbene Chemistry," Academic Press, New York, 1964; D. Bethell, *Adv. Phys. Org. Chem.*, 1969, **7**, 153.

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[4] *Cf.* D. R. Dalton and S. A. Liebman, *Tetrahedron*, 1969, **25**, 3321.

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