

SOLVENT EFFECT ON THE QUANTUM YIELD FOR PHOTOCHEMICAL  
CLEAVAGE OF DIAZOKETONES <sup>1</sup>

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The photolysis of a group of diazocompounds has been recently studied quantitatively <sup>2a</sup>; a reaction mechanism was suggested involving as primary act nitrogen elimination with formation of carbeno intermediates <sup>2</sup>. The influence of molecular structure on quantum yield was interpreted as implying limiting forms with a large degree of charge separation. As to the medium effect, qualitative informations on diphenyldiazomethane were inferred from a study of the final products of photolysis, therefore relating to the global process of cleavage <sup>2b</sup>.

Following previous kinetic, infrared and mass-spectrometric measurements <sup>3</sup>, it seemed of interest to get some informations on the solvent effect for the primary act of photolysis of some suitably chosen diazocarbonyl compounds.

The irradiations have been made with a Bausch and Lomb grating monochromator (linear dispersion 66 Å/mm in the first order) and a Hanovia mercury arc source of high intensity; a potassium ferrioxalate actinometer has been used throughout. The excitation condi-

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<sup>2a</sup> W. Kirmse and L. Horner, Ann. **625**, 34 (1959); <sup>b</sup> L. Horner et al., Ann. **573**, 17 (1951); **614**, 19 (1958); Chem. Ber. **85**, 225 (1952).

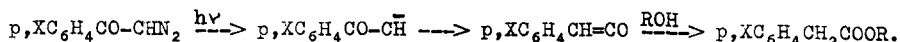
<sup>3</sup> A. Foffani, L. Salvagnini and C. Pecile, Ann. Chim. (Rome) **49**, 1677 (1959); A. Foffani, B. Cantone, S. Pignataro and F. Grasso, Nuovo Cimento (1963), in press; A. Foffani, C. Pecile and S. Ghersetti, Tetrahedron **11**, 285 (1960); **14** (1963), in press

tions were of total absorption of radiation; the extent of decomposition was followed at time intervals with an Optica CF4 grating spectrophotometer, after dilution of the solutions; both for the excitation and for the kinetic measurements, the region of peak absorption of the diazocompounds near 300  $\mu$  was used, excluding in this way any appreciable contribution to the absorption from the photolysis products.

In such conditions, the quantum yields here reported clearly refer to the primary photochemical act. Preliminary experiments on each side of the 300  $\mu$  maximum, as well as on the band at 250  $\mu$ , did not show any wave-length effect on the quantum yield within the limits of experimental error (4 experiments in methanol at 250, 278, 294 and 313  $\mu$  gave an average value of  $0.46 \pm 0.02$  for the quantum yield). It may be pointed out in this respect that qualitative informations by L. Horner <sup>2a</sup> in the region of the presumed  $n-\pi^*$  transition, which in our case appears as a weak shoulder near 370  $\mu$ , do seem to indicate instead a remarkable lowering of quantum yield.

The compounds studied were diazoacetophenone and its para methyl-, methoxy-, chloro- and nitro-derivatives and phenylbenzoyldiazomethane; for their preparation, see ref. 3. The solvents used were Erba RP or RS grade, purified when necessary via standard methods.

The table gives the results obtained in methanol and n-hexane and - for the diazoacetophenone and its p,methyl derivative - in solvents of varying polarity. It was admitted <sup>2</sup> that the carbene intermediate formed in the primary photolytical act gives a ketene, by a Wolff rearrangement; depending on the medium, the ketene can be isolated as such, or it can dimerize or react with the solvent. In particular, in hydroxylic media it forms an ester of the homologue acid, e.g. for the diazoacetophenones:



It should be noted that by changing the solvent these compounds undergo a fairly typical variation of the relative intensity of the two main bands at 250-300  $\mu$ , with a bathochromic shift in polar

TABLE

Solvent effect on  $\lambda_{\max}$  at 300  $\mu$  and on quantum yield for the photolysis of diazoacetophenones.

X	n-hexane <sup>a</sup>		ethyl acetate		ethanol		methanol		water-ethanol 80 - 20%	
	$\lambda_{\max}$	$\phi$	$\lambda_{\max}$	$\phi$	$\lambda_{\max}$	$\phi$	$\lambda_{\max}$	$\phi$	$\lambda_{\max}$	$\phi$
H	(277)	0.55	295	0.44	297	0.45	294	0.46	298	0.40
CH <sub>3</sub>	(286)	0.62	295	0.39	298	0.39	296	0.41	301	0.30
CH <sub>3</sub> O	283	0.50					304	0.34		
Cl	(287)	0.62					299	0.41		
NO <sub>2</sub>	299	0.31					307	0.18		

<sup>a</sup> Some figures in n-hexane are in parenthesis as they refer to ill-defined peaks or shoulders.

media, as observed for the corresponding acetophenones <sup>4</sup>.

The substituent and solvent effects on the spectra (mainly on the frequencies) can be explained as substantially due to interactions of mesomeric type, probably more active in the excited electronic state; this explanation is based on the analogies with the spectra of the corresponding acetophenones, taking however into account the fact that in this case the charge distribution in the electronic states is likely to be markedly influenced by the diazgroup. In this respect it may be observed that the substituent effects on the I.R.  $\nu_{\text{NN}}$  are very small <sup>3</sup>, except in the case of more drastic modifications of structure; as to the  $\nu_{\text{CO}}$ , the substituent effect involves a frequency range larger than for acetophenones <sup>4</sup>, again reflecting an influence of diazgroup in the electronic distribution.

The rate of nitrogen elimination appears to be affected in a similar way because the para-substituents cause a general lowering in the quantum yield almost independently from the nature of the solvent

<sup>4</sup> W.F. Forbes et al., Can. J. Chem. 35, 488, 1049 (1957).

(see data in methanol and n-hexane; the figures in methanol are in good agreement with the ones given by Horner <sup>2a</sup>) <sup>5</sup>.

These values, together with those obtained for diazoacetophenone and its p,methyl-derivative in different solvents, show a notable lowering of quantum yield in polar and hydroxylic media. Other non quantitative experiments carried out in aqueous ethanol on the same diazoketones have also revealed a slight but definite reaction rate lowering on increasing the water content in the range 0 + 85%.

In the literature there are to be found only a few sufficiently detailed studies as to the solvent effect on the quantum yield of photochemical reaction; the informations obtainable are often fragmentary and difficult to compare <sup>6</sup>. Often the work deals with the effect of the solvent on the global reaction, which may lead to final products of different nature by the intervention of varying mechanisms according to the type of solvent (see for instance Horner's work on diphenyldiazomethane <sup>2b</sup>). The medium effect on the primary step of photolysis is generally more difficult to be interpreted because it implies, in addition to solvent polarization phenomena in the fundamental and excited states, other less clear effects on the electronic transitions in question and on the redistribution of excitation energy followed by radiative or non radiative

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<sup>5</sup> A recent attempt [H. Ziffer and N.E. Sharpless, J. Org. Chem. 27, 1944 (1962)] to correlate the Horner's data for the substituent effect on quantum yield in methanol with the Hammett equation, seems to indicate a satisfactory correlation on plotting  $\log \phi \cdot \epsilon$  vs.  $\sigma$ , although its significance is somewhat uncertain. Our results in n-hexane, while roughly confirming the plot in methanol, are obviously insufficient to support the type of trend proposed.

<sup>6</sup> see for instance D. Schulte Frohlinde, Ann. 615, 114 (1958); D. Booth and R.M. Noyes, J. Am. Chem. Soc. 82, 1868 (1960); G.A. Strongin, Trudy Khim. i Khim. Tekhnol. 2, 141 (1959); 3, 398 (1960); 4, 419 (1961) [see C.A. 54, 10906e (1960); 55, 25799e (1961); 56, 62f (1962)].

conversion processes.

The primary stage of photolysis, with which the present measurements are concerned, is presumably the same in the different solvents; it is therefore to be expected that the influence of the medium may be interpreted on the basis of a varying extent of conjugative phenomena and of the intervention of limiting forms suitable to cause an excitation energy redistribution favourable to dissociation; this interpretation may be proposed both for the substituent and solvent effects.

The prevalence of mesomeric effects on the quantum yield is also suggested by the above mentioned parallelism between the trend of the U.V. spectra and of the photolytical yield, in the sense that a large mesomeric effect would explain both the bathochromic shift and the intensity change of the bands <sup>4</sup> and that such a behaviour is accompanied by a relevant yield lowering in any case (see also above). Moreover the observed independence of the quantum yield on the wavelength in a large interval suggests that the solvent effect on the excitation energy is not likely to influence appreciably the quantum yield.

Finally we tried to test whether the substitution of the hydrogen atom of the  $-CHN_2$  group might cause any variation in the nature of the medium effect. To this aim we studied phenylbenzoyldiazomethane. The situation is here somewhat involved owing to the thermal decomposition in solution, except in media of low dielectric constant. Anyway, in those solvents where quantum yield determinations have been possible, the medium effect appears to be little affected by phenyl substitution.