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THE INTERACTION OF DIAZOCARBONYL COMPOUNDS WITH HYDROXYLIC SOLVENTS*

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Abstract—In accordance with previous results, additional spectral evidence is given for the effect of the medium on the nature of solvent interactions for diazocarbonyl compounds.

Comparative frequency, integrated intensity and half-width measurements for the diazo band in diazohydrocarbons and diazoketones show that the frequency and intensity values are substantially unaffected on going from apolar solvents to typically polar solvents or those capable of interacting with hydrogen bonds. The intensity changes previously reported appear to correspond only to half-width changes of the band, and they are particularly strong in the case of diazoketones. The possible occurrence of enolic or isodiazo forms seems to be ruled out in the cases considered, both on the basis of the above facts and the ultraviolet behaviour of these substances, the variations observed being through changes in the medium even in the absence of hydrogen atoms capable of transposition.

However, an explanation only on the basis of the intervention of intermolecular interactions through hydrogen bonds presents some difficulties, as the variations observed for the intense band around 250 mμ are not of a type normally occurring in these cases.

The infrared study has been extended to an examination of the effect of hydroxyl and amino ligands on the carbonyl band of aliphatic and aromatic diazoketones, and the corresponding behaviour of the O—H and N—H stretching bands of the ligands. In particular it has been observed that there are two bonded-carbonyl bands for singularly low values of the ratio ligand to diazoketones, such as to rule out the occurrence of polymeric associations.

These and other facts in the ultraviolet and infrared behaviour are reasonably consistent with the possible intervention of conformational isomeric forms. The relative stability of these forms appears to be particularly sensitive both to intramolecular electronic and field effects and to intermolecular interactions of the carbonyl group, which are likely to modify the molecular charge distribution.

IN THE course of infrared intensity measurements on diazo compounds,[1] solute–solvent interaction effects have been observed, the further study of which is of interest in the light of recent results on the effect of medium in the ultraviolet for diazocarbonyl compounds[2] and the apparent intensity changes for the diazo stretching band in their infrared spectra.[3]

The explanations given for the two effects are very different: (a) The infrared results, which seemed to indicate an intensity invariance of the carbonyl band and a decrease of the diazo one on going from apolar to hydroxylic solvents, should apparently rule out the presence of a keto-enolic equilibrium, pointing rather to the

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[1] A. Foffani, C. Pecile and S. Ghersetti, *Tetrahedron* **11**, 285 (1960).

[2] E. Fahr, *Chem. Ber.* **92**, 398 (1959).

[3] F. A. Miller and W. B. White, *J. Amer. Chem. Soc.* **79**, 5974 (1957).

possible occurrence of isodiazo forms. Forms of this type have already been suggested in order to explain some features of the low-temperature infrared spectrum of diazomethane,[4] and chemical evidence has been put forward in favour of the isodiazo form;[5] (b) The ultraviolet spectra do not support the previous interpretation, in so far as their variation through medium effect is observed even in the absence of hydrogen atoms capable of producing enolic or isodiazo tautomeric forms. However, an explanation only on the basis of the intervention of intermolecular interactions through hydrogen bonds presents some difficulties, because the variations observed for the intense band around 250 mμ are not of a type generally occurring in these cases,[6] and do not imply a simple shift to lower frequencies but a splitting of the band.

EXPERIMENTAL

The conditions for intensity measurements, their limit of accuracy and the preparation and purification of the diazo compounds were in accordance with Föffani *et al.*[1] A Perkin Elmer mod. 112 infrared spectrometer with CaF_2 optics was employed throughout, taking care to eliminate atmospheric water vapour. The solvents were purified by standard methods. The ultraviolet measurements were performed with an Optica CF4 single-beam instrument.

TABLE 1. SOLVENT EFFECT ON THE DIAZO STRETCHING VIBRATION OF DIAZOACETOPHENONE

Solvent	ν(NN) cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$\varepsilon_{max} \times 10^{-3}$	$A_{NN} \times 10^{-4}$
n-Hexane	2108	11	1·27	5·4
CCl_4	2108	14	1·12	5·8
C_2Cl_4	2108	13	1·15	5·2
CH_2Cl_2	2109	18	0·93	6·0
$CHCl_3$	2111	18	0·87	5·6
n-Butanol	2108	22	0·75	5·9
CH_3NO_2	2112	18	0·91	6·1
KBr	2108			

A = Integrated intensity in mole^{-1} liter cm^{-2}

ε = Apparent peak extinction coefficient in mole^{-1} liter cm^{-1}

RESULTS AND DISCUSSION

Tables 1 and 2 give the data so far obtained on the effect of medium on frequency, integrated intensity and half-band width for the diazo stretching band in diazohydrocarbons and diazoketones. The frequency shifts observed are very small, and also the intensity does not change significantly on going from apolar solvents to typically polar ones or to those capable of interacting through hydrogen bonds. Correspondingly the half-width of the band increases strongly, particularly for the last mentioned solvents. It is relevant that for solvents previously investigated (CH_2Cl_2 and n-butanol) the intensity change reported[3] corresponds to a decrease in the peak absorption coefficient; on the other hand Table 1 shows that there is a substantial invariance of the integrated intensities even for solvents in which $\Delta\nu^a_{1/2}$ variation reaches a 1:2 ratio.

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[4] D. E. Milligan and G. C. Pimentel, *J. Chem. Phys.* **29**, 1405 (1958); T. D. Goldfarb and G. C. Pimentel, *J. Amer. Chem. Soc.* **82**, 1805 (1960).

[5] E. Müller and D. Lundesteck, *Chem. Ber.* **87**, 1887 (1954).

[6] see for example: G. C. Pimentel and A. L. McClellan *The Hydrogen Bond* (Edited by W. H. Freeman) pp. 157 *et seq.* San Francisco (1960).

It follows that the basic parameters for the diazo band, frequency and integrated intensity, are almost medium-invariant; which is supported by previous ultraviolet results,[2] ruling out the intervention of isodiazo forms involving tautomerism to diazo group; as their presence in significant amounts should cause a substantial intensity decrease of the band. It is evident from Table 2 that the $\Delta\nu^{a}_{1/2}$ increase from CCl_4 to n-butanol is within 10–30% for the diazohydrocarbons, reaching 80–90% for the diazocarbonyl derivatives: such a difference in behaviour could certainly not be caused by tautomerism, as it is also observed for phenylbenzoyldiazomethane where no hydrogen atoms are available; and, therefore, it may be connected with the prevailing influence of hydrogen bonds on the diazocarbonyl compounds and dipole–dipole interaction effects.

TABLE 2. EFFECTS OF HYDROXYLIC SOLVENTS ON THE FREQUENCY, SHAPE AND INTENSITY OF THE DIAZO AND CARBONYL STRETCHING VIBRATIONS IN DIFFERENT DIAZOHYDROCARBONS AND DIAZOKETONES

Compound	Solvent	$\nu(NN)$ cm^{-1}	$A_{NN} 10^{-4}$	$\Delta\nu^{a}_{1/2}$ cm^{-1}	$\nu(CO)$ cm^{-1}
$C_6H_5CHN_2$	CCl_4	2061	4·2	9	
	n-Butanol	2060	5·4	12	
$(C_6H_5)_2CN_2$	CCl_4	2041	7·6	11	
	n-Butanol	2040	7·7	12	
CH_3COCHN_2	CCl_4	2108	4·5*	12	1662
	n-Butanol	2110	5·0	22	1662sh, 1643sh, 1633
$C_6H_5COCHN_2$	CCl_4	2108	5·8	14	1633, 1622sh
	n-Butanol	2108	5·9	22	1628sh, 1618sh, 1609
$C_6H_5COC(C_6H_5)N_2$	CCl_4	2073	5·3	14	1636, 1621sh
	n-Butanol	2077	5·8	24	

A = Integrated intensity in $mole^{-1}$ liter cm^{-2}

* Uncorrected for the contribution of a weaker band at 2090 cm^{-1}.

The infrared study was extended to the effect of hydroxylic and amino ligands on the carbonyl band of diazoacetone, the latter being particularly suitable owing to the absence of interference from phenyl bands in the carbonyl region. Fig. 1 shows in the O—H stretching region the behaviour of diazoacetone, diazoacetophenone and phenylbenzoyldiazomethane in CCl_4 solutions in the presence of phenol with 20/1 diazoketone/phenol ratio. Fig. 2 shows the behaviour of the carbonyl stretching band of diazoacetone in C_2Cl_4 solution by addition of phenol in 1/1 to 10/1 phenol/diazoacetone ratios, and in n-butanol solution.

The behaviour of the phenolic O—H band (Fig. 1) is normal for an hydrogen bond interaction with a ketone (see for example[7]). A similar situation occurs for a diazoacetone + pyrrole solution in CCl_4; with 10/1 diazoacetone/pyrrole ratio a free N—H band at 3495 cm^{-1} and a bonded N—H one around 3390 cm^{-1} was observed.

In the system diazoacetone–phenol–tetrachlorethylene as from Fig. 2 the behaviour in the carbonyl region for 2/1 phenol/diazoacetone ratio two somewhat broad peaks appear at 1643 and 1633 cm^{-1} in addition to the main 1662 cm^{-1} band; on increasing the phenol/diazoacetone ratio the intensity of the two peaks increase while the high-frequency one decreases, although the frequencies do not change appreciably. Also

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[7] N. Fuson, P. Pineau and M. L. Josien, *J. Chim. Phys.* **55**, 454 (1958).

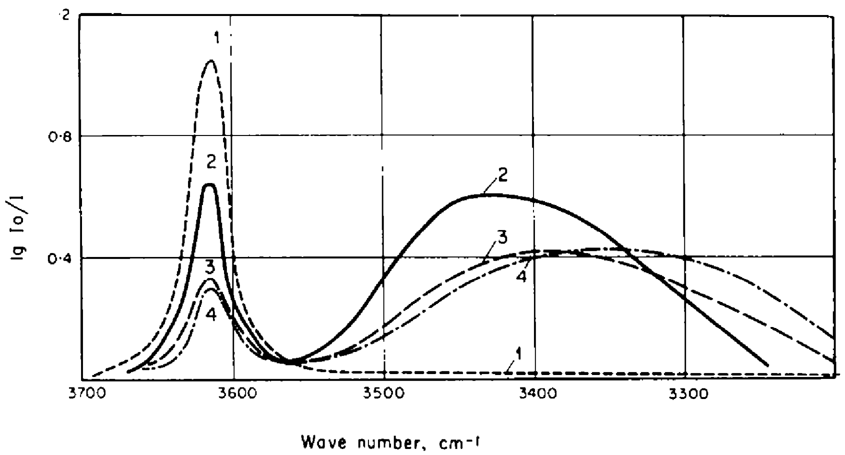

FIG. 1. Behaviour of phenol ν(OH) stretching vibration in presence of diazoketones
Curve 1: Phenol $4 \cdot 10^{-3}$ M in CCl_4
Curve 2: as above + $8 \cdot 10^{-2}$ M $C_6H_5COC(C_6H_5)N_2$
Curve 3: as above + $8 \cdot 10^{-2}$ M $C_6H_5COCHN_2$
Curve 4: as above + $8 \cdot 10^{-2}$ M CH_3COCHN_2
Cell thickness: 1 cm.

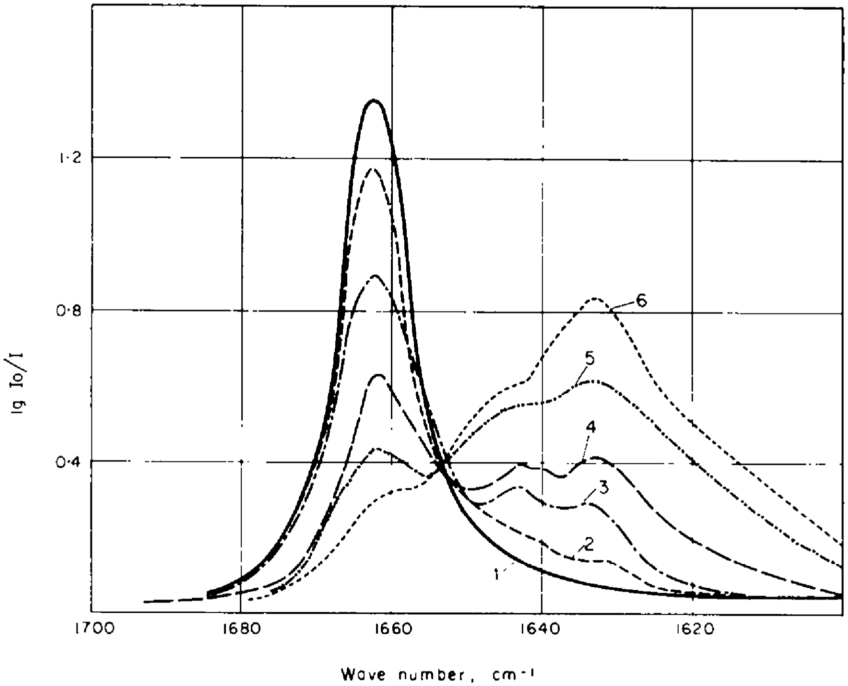

FIG. 2. Influence of hydroxylic media of different composition on the carbonyl band of diazoacetone
Curve 1: Diazoacetone 10^{-2} M in C_2Cl_4
Curve 2: as above + 10^{-2} M phenol
Curve 3: as above + $2 \cdot 10^{-2}$ M phenol
Curve 4: as above + $5 \cdot 10^{-2}$ M phenol
Curve 5: as above + 10^{-1} M phenol
Curve 6: Diazoacetone 10^{-1} M in n-butanol
Cell thickness: 1 mm for curves 1 to 5; 0·1 mm for curve 6.

in n-butanol the position of the peaks is unchanged and the high-frequency one is present as a shoulder.

The effect of pyrrole on the CO band of diazoacetone in C_2Cl_4 is normal for carbonyl bands in cases of weak interactions: the CO band is broadened to lower frequencies without the appearance of distinct peaks.

The 1662 cm^{-1} band for diazoacetone in an inert solvent is clearly assignable as the free-carbonyl stretching mode; the one observed in the same position in the presence of phenol, the intensity of which regularly decreases by addition of phenol, is again to be assigned to the residual non-associated form and may also be observed,[8] although much weakened in n-butanol solution.

The fact that the other two bands, apparently connected with different environmental situations of the carbonyl, already appear at low phenol/diazoacetone ratios, shows that the one with lower frequency is not caused by phenol-diazoacetone associations having 2/1 or higher molar ratios. For example, in the case of benzophenone, associates of this kind are observed only for ethanol/ketone ratios higher than 25/1;[8] which is similar in other cases,[9] although less accurately described.

Rotational isomeric forms, the relative stability of which may be markedly affected through intramolecular electronic effects and intermolecular interactions with the carbonyl group may also be considered as influencing these diazocarbonyl compounds. It may be noted in this connection that [1,10] for the diazocarbonyl compounds the CO stretching frequency appears to be markedly low (1630–1660 cm^{-1}), owing to the prevailing intervention of mesomeric forms extended to the carbonyl group and involving a relevant degree of charge separation; resulting in a significant increase for the bond order of the C—C bond between the carbonyl and the CNN group. Also a carbonyl-diazo group field interaction may be of significance.

For diazoacetone the present experimental evidence indicates the presence of two bonded-carbonyl bands, tentatively assigned to the two conformational isomers, although only one is observed for the free carbonyl; correspondingly only one band is found in the ultraviolet spectrum of diazoacetone in an apolar solvent (Fig. 3). The predominance of one form for diazoacetone in inert solvents is not unique, this being consistent with cases of $\alpha\beta$-unsaturated carbonyl systems recently reported.[11] A diazoacetophenone solution in CCl_4 (Table 2) shows a 1633 cm^{-1} band and a shoulder at 1622 cm^{-1}, which might correspond to the second isomeric form. The ultraviolet spectrum (Fig. 3) shows an additional lower frequency band in inert solvent but a phenyl-type band may interfere with the absorption due to a second isomeric form.

In n-butanol, diazoacetophenone shows two shoulders at 1628 and 1618 cm^{-1} and a strong band at 1609 cm^{-1}; the latter is probably a bonded-carbonyl band, while the shoulders might be assigned as the free-carbonyl bands shifted by about 5 cm^{-1} through solvent effect. The second bonded-carbonyl band does not appear, presumably due to interference with phenyl modes. In diazoacetophenone also, therefore, the ligand apparently affects the equilibrium between the two forms.

The behaviour of phenylbenzoyldiazomethane is essentially similar: although

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[8] R. S. Becker, *J. Mol. Spectroscopy* **3**, 1 (1959).

[9] J. Dercosch, *Monatsh.* **90**, 645 (1959); ref. [6] pg. 135 et seq.

[10] E. Fahr, *Liebigs Ann.* **617**, 11 (1958).

[11] K. Noack, *Spectrochim. Acta* **18**, 1625 (1962) and ref. therein.

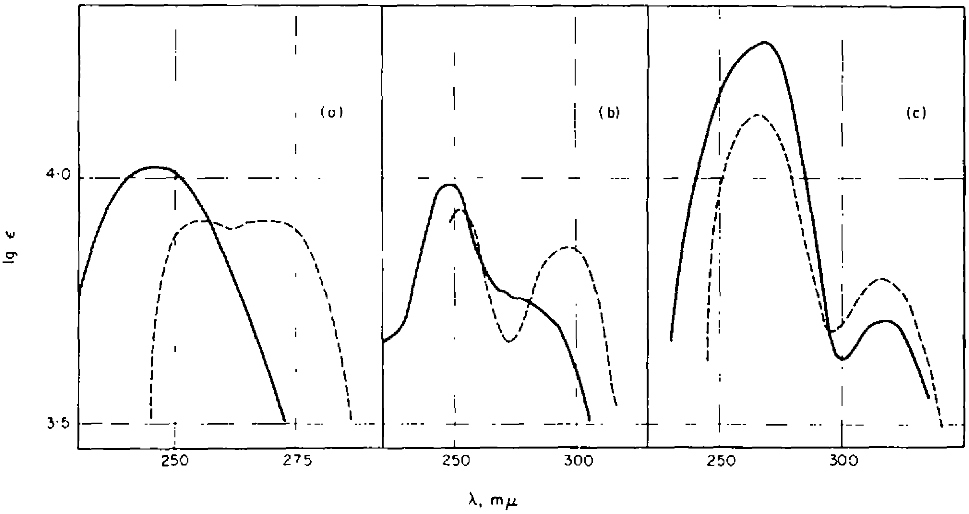

Fig. 3. Ultraviolet spectra of (a) diazoacetone, (b) diazoacetophenone, (c) phenylbenzoyl-diazomethane in cyclohexane (solid line) and n-butanol (broken line).

the shoulders cannot in this case be localized with certainty. In CCl_4 there is a band at 1636 cm^1 with a shoulder at 1621 cm^{-1}; in n-butanol there is a somewhat complex band around 1615 cm^{-1} with shoulders not well defined at higher frequencies. The analogy with diazoacetophenone again supports the view that tautomerism is not the determining factor in the explanation of the facts observed.*

The solid spectra of diazoacetophenone (with a shoulder at 1618 cm^{-1} and a stronger band at 1607 cm^{-1}) and of phenylbenzoyldiazomethane (where only a sharp band at 1620 cm^{-1} is observed) are consistent with the features of the solution spectra and suggest the presence in the solid of that form which in solution gives the lower frequency band. However, for diazoacetophenone the possibility of a single band splitting through solid state interference must be considered.

As previously stated, the ultraviolet spectra of the diazocarbonyl compounds in different media—as shown by Fahr[2]—rule out the intervention of tautomeric equilibria, but the possibility of its interpretation on the basis of simple intermolecular interactions via hydrogen bonds in the case of hydroxylic solvents is uncertain. The typical effect observed is a gradual decrease in intensity of the band at 240–260 mμ by hydroxylic solvent addition, while at the same time a band of similar intensity does appear gradually at 270–280 mμ. This is, for example, the situation for simple diazoketones or for double ones with the diazogroups separated by an open aliphatic chain,[2,3] but such a doubling is not observed for diazoesters[3] and cyclic diazoketones with vicinal diazogroups.[2] In aromatic systems a phenyl-type band should partially superimpose the observed effect, but its interference may not be of such an amount as to justify *per se* the solvent effect observed. The spectral behaviour may well be illustrated by reference to the simple series of diazoketones: diazoacetone,

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* Of particular interest in this regard should be the study of the sterically hindered aliphatic compound $(CH_3)_3CCN_2COC(CH_3)_3$.[12]

[12] M. S. Newman and A. Azkell, *J. Org. Chem.* **24**, 385 (1959).

phenylbenzoyldiazomethane, whose spectra in cyclohexane and n-butanol are reported in Fig. 3. The spectra of phenylbenzoyldiazomethane confirm that the occurrence of tautomeric forms does not explain the facts observed, owing to the absence of hydrogen atoms capable of transposition; but the experimental pattern cannot be interpreted only on the basis of intermolecular interaction effects with the hydroxylic solvent for the reasons previously shown, considering also that the infrared behaviour points to a normal character for those interactions. For diazoacetone a weak band ($\lg \varepsilon = 1{,}21$) is also present at 365 mμ in cyclohexane, showing a normal behaviour in hydroxylic media with a shift to higher frequencies, assignable as an $n - \pi^*$ transition.

A tentative explanation of these facts on the basis of the possible occurrence of some kind of rotational isomerism, as before proposed to interpret the appearance of two bands for free or bonded-carbonyl in the diazocarbonyl compounds, seems reasonable and it might also justify the marked broadening of the NN stretching band in the infrared spectrum. In support of this is the absence of the medium effect in cyclic diazoketones[2] and in acidic azides,[13] both cases where the possibility of conformational isomerism is clearly ruled out. This interpretation is obviously to be tested among others by a study of the temperature effect on the ultraviolet and infrared absorption bands. For the compounds with CHN_2 grouping deuteration should permit the estimation of the possible occurrence of coupling effects involving the carbonyl, which might be likely to cause a solvent-sensitive splitting. Useful information should also come from an NMR study in systems where a conformational equilibrium might take place.

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[13] P. Grammaticakis, *C. R. Acad., Sci. Paris* **244**, 2517 (1957).