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SPECTROPHOTOMETRIC STUDIES ON SOME 1-(ARYLAZO)-PROPANE-2-ONE.

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SPECTROPHOTOMETRIC STUDIES ON SOME 1-(ARYLAZO)-PROPANE-2-ONE.

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SUMMARY

The UV and visible absorption spectra of some 1-(arylazo)-propane-2-one are investigated in different organic solvents. The spectra are discussed in terms of medium effects and molecular structure. Band assignment is also attempted. The variation of absorption spectra with pH is utilised for the determination of pKa. The effect of substituents on pKa, λ_{max} and ε_{max} is also considered. The important bands is the ir-spectra are discussed in relation to molecular structure.

INTRODUCTION

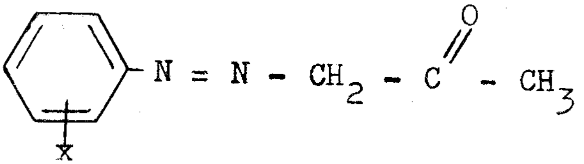
The absorption spectra of azo compounds were the subject of several investigations[1-4]. The longer wavelength band (located in the visible region) was assigned to n–π* transition by Jaffe[1] while Korner[2] applying the Hukel molecular orbital calculations (HMO) attributed this band to π—π* and n—π* transitions. Issa[3] assigned this band to π—π* transition within the azo group influenced by intramolecular charge transfer. The ir-spectra of azo dyes were extensively studied[5] and the relation between N=N and molecular structure was investigated[6].

The present work includes the investigation of absorption spectra of some azo dyes containing the acetonyl moiety in organic solvents of different polarities and buffer solutions of varying pH values. The ir-spectra were studied as KBr discs, the main bands are assigned to their vibrational modes.

EXPERIMENTAL

The azo dyes involved in the present investigation were prepared as previously reported[7]. The solvents used for spectral measurements were purified by recommended procedures[8]. Britton and Robinson[9] universal buffer solutions were prepared and used to control ionic strength and pH. The infrared spectra were recorded as KBr discs with the aid of a PYE UNICAM SP 1000 spectrophotometer. The UV-spectra were obtained by a PYE UNICAM SP 800 spectrophotometer.

The compounds under investigation have the general structural formula:



where x = H (I), p-OCH_3 (II), p-CH_3 (III), p-Cl (IV), p-Br (V), p-COOH (VI), p-NO_2 (VII), m-NO_2 (VIII), o-NO_2 (IX) and o,p-dinitro (X).

RESULTS AND DISCUSSION

Infrared Spectra

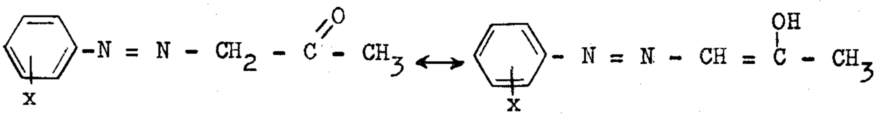
The important bands in the IR-spectra for the compounds under investigation are reported in Table (1). A strong broad band with varying intensity appears in the spectra of all compounds in the 3220–3290

Table 1. Solid state infrared spectral data for 1-(arylazo)-propane-2-one as KBr discs.

$\bar{\nu}$ cm^{-1}										Band Assignment
I	II	III	IV	V	VI	VII	VIII	IX	X	
3280	3270	3275	3260	3260	3220	3280	3275	3280	3285	ν OH
3160	3155	3155	3120	3140	3130	3160	3160	3165	3115	ν CH_{asym}
3090	3070	3060	3090	3060	3060	3110	3100	3105	3050	ν CH_{sym}
1665	1673	1670	1700	1680	1695	1690	1680	1685	1705	C=O
1615	1610	1620	—	1610	1615	1620	1615	1610	1630	C=C
1600	1605	1610	1600	1598	—	1610	1610	1600	1608	C=C
1540	1555	1560	1585	1560	1560	1575	1565	1570	1585	C=C
1505	1500	1515	1490	1495	1513	1505	1510	1500	1512	C=C
1400	1405	1403	1410	1415	1395	1400	1420	1415	1430	ν N=N
1290	1320	1315	1320	1305	1318	1340	1325	1320	1330	ν C—N
760^5	820^2	820^2	832^2	825^2	830^2	843^2	880^1	775^4	882^1	γ CH
698^5	—	—	—	—	—	—	810^3	—	855^2	γ CH

1,2,3,4 and 5 denoting the number of adjacent ring hydrogen atoms.

cm^{-1} region. The band corresponds to the stretching frequency of the hydroxyl group (ν OH). The presence of this band denotes the possible existence of a tautomeric shift of the type:



If x is an electron donor, the band position exhibits an apparent low frequency value relative to the parent compound while electron acceptor groups cause a slight counter shift. This behaviour indicates that the acceptor groups favour the stabilization of the enolic form. The band due to the ν_{CH} of methyl group is observed in the region 3165–3050 cm^{-1} with almost two peaks for the asymmetric and symmetric modes. The band due to the stretching frequency of the C=O group appears in the 1665–1705 cm^{-1} region. The strong band located near 1615 cm^{-1} corresponds probably to stretching vibration of the ethylinic bond overlapped with that due to the ν_{asym} N=N group. The existence of this band is also a further support for the keto-enol tautomerism. The band located near 1400 cm^{-1} can be assigned to the symmetric N=N stretching[10]. This band shifts to higher wavenumber with acceptor substituents which goes in accordance with increased overlap of the molecular orbitals of the N=N system and decreased participation of the enolic form. The C–N band appears around 1300 cm^{-1} while the γ_{C-H} can be observed below 1000 cm^{-1}.

Spectra in Ethanol

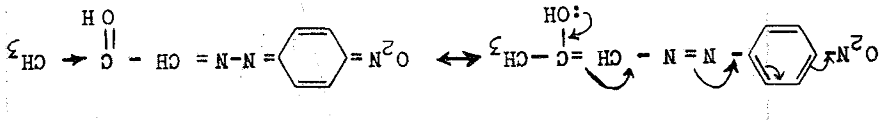
The spectra of the azo dyes investigated in ethanol (Table 2) comprise mainly three absorption bands within the 235–450 nm region. The first band located near 250 nm is assigned to the π–π^* transition of the phenyl residue, namely the ^1L_b transition[4], this band shows the general trend being red shifted relative to the unsubstituted compound (I), where the substituent is an electron donor or acceptor. However, donor substituents cause a larger shifts compared to acceptor ones. The second band is observed around 300 nm. Intensity and position of the band are dependent on the molecular structure. The band is generally broad and splits into two bands in the spectra of II and III where the substituent

Table 2. Absorption bands in ethanol.

No	^1L_b		$\pi - \pi^*$ C=O +N=N		C.T. band	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
I	238	1.11	297	0.58	350	2.15
II	236	1.28	302	0.91	366	4.90
			313	0.88		
III	241	1.03	293	0.68	360	1.80
			303	0.55		
IV	255	0.59	307	0.81	358	1.18
V	235	0.93	304	0.66	356	1.89
VI	252	0.61	301	0.36	358	1.91
VII	240	1.00	293	0.38	380	3.05
VIII	250	1.23	320	0.71	420	0.64
IX	225	0.83	277	0.53	395	1.72
			319	0.54		
X	256	0.75	270	0.53	358	1.68

$\varepsilon_{max} = x\ 10^{-4}$, λ_{max} = nm

(x) is electron donor. On the other hand the spectrum of IX exhibits two bands with maximum absorption at 277 and 319 nm while the spectrum of X displays one band at 270 nm. The other band suffers a bathochromic shift and is obscured by the most intense band located near 356 nm. The band at shorter wavelength can be assigned to the π–π* transition of the carbonyl group while that at longer wavelength is attributed to the π–π* transition of the azo group. The two bands overlap and appear as a broad band of low absorptivity in compounds containing the electron acceptor groups. The existence of the nitro groups favour the enol form. The case which increases the energy of occupied π- orbitals of the azo group (red shift) meanwhile, decreases the energy of occupied π– orbitals of the carbonyl group (blue shift). On the other hand, the electron donor groups cause a red shift for both bands. The band on the longer wavelength side, located within the 360–450 nm range displaying a high molar absorptivity can be assigned to intramolecular charge transfer interaction (CT). The unsubstituted compound shows this band at 350 nm, compounds II–VI exhibit this band at the same position or slightly red shifted. The CT originates from the phenyl ring to the N=N center influenced by the acceptor character of the carbonyl group The magnitude of the CT is affected by the nature of the substituent. The spectra of compounds VII, VIII and IX containing nitro group show this band at 380, 420 and 395 nm respectively. The presence of the nitro group favours the formation of the enolic form and the CT originates in such structures from the OH group to the nitro group. In this case the methyl group favours the CT to the nitro group while in the case of compounds deprived of the NO_2 group, the $+I$ effect of the methyl group antagonises the CT to the carbonyl group:



The variation of λ_{max} of the CT band with the σ (Hammett constant) Figure 1 results in a broken line with its inflection at $x = H$. The plot indicates that the band shifts to red by increasing the acceptor or donating character of the substituent. However, the magnitude of the shifts is larger in case of the acceptor substituents than in case of the donor ones.

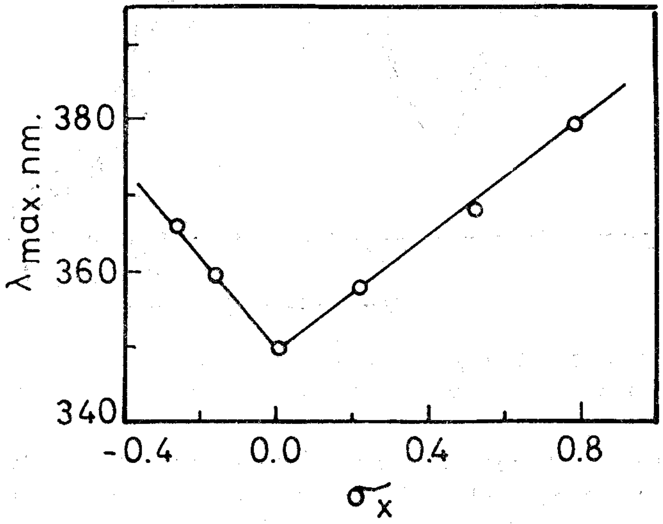


Fig. (1). Relation between λ_{max} nm and σ_x.

Solvent Effect on Absorption Spectra

Intramolecular CT bands are solvent sensitive while local transition bands are relatively insensitive to change of solvent. The absorption spectra of the p-methoxy-derivative (II) in organic solvents of varying polarities are shown in Figure 2, practically no shift is observed due to change of solvent from cyclohexane to ethanol for the ^1L_b band (Tables

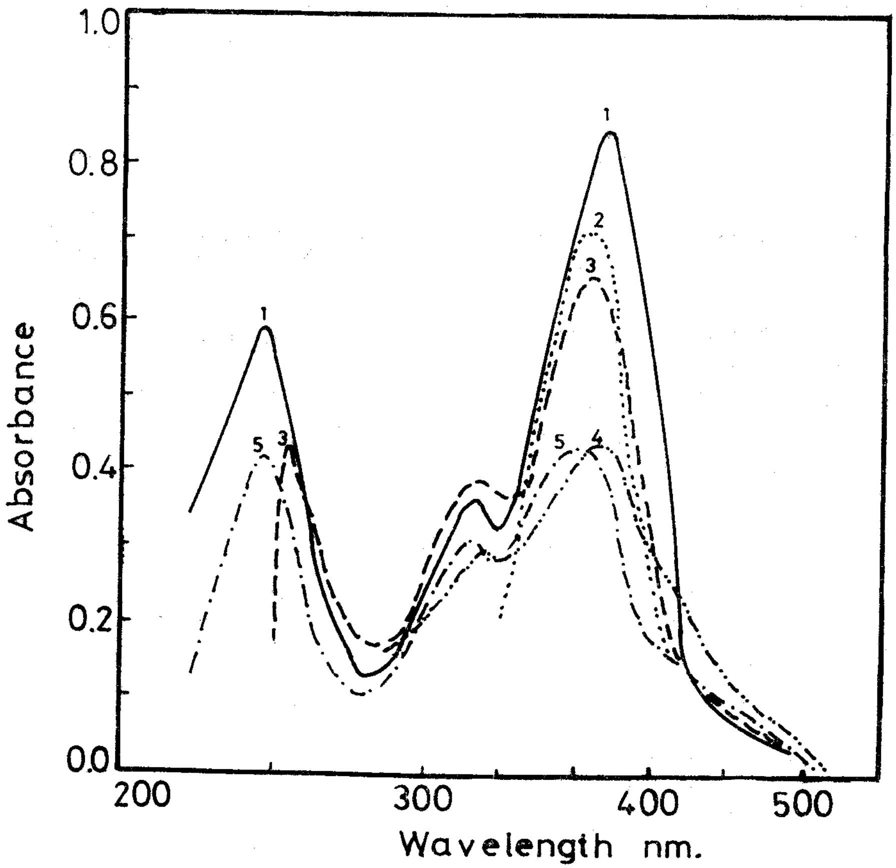


Fig. (2). Absorption spectra of 1–(p–methoxyphenylazo)–propane –2–one in organic solvents 1– Ethanol, 2– Acetone, 3– Chloroform, 4– Carbontetrachloride and 5– Cyclohexane

2 and 3). The second band suffers a slight red shift in ethanol. However, the protic solvents cause blue shift and the non protic solvents cause red shift. Generally, the shift in band position is the net resultant effect of the red shift due to increased polarity of the solvent and the blue shift due to increased solvent stabilization of the ground state of the azo center. The CT band shifts to red on going from cyclohexane, CCl_4, acetone, $CHCl_3$ to ethanol. The red shift is due to dipole-dielectric interaction as well as hydrogen bond formation. In some cases, hydrogen bonding is much stronger than the dielectric effect. Figure (3) shows that λ_{max} of the CT band varies more or less linearly with f (D)[11], where

$$f(D) = 2(D-1)/2D + 1$$

The slight deviation from linearity in the λ_{max} — f(D) plots is often taken as an evidence for hydrogen bond formation between solute and solvent molecules.

Table 3. Absorption bands in organic solvents.

No.	solvent	band A		band B		band C	
		λ_{max}	logε	λ_{max}	logε	λ_{max}	logε
I	acetone					340	3.22
	$CHCl_3$			290	2.79	342	3.23
	CCl_4			297	2.94	334	3.28
	C_6H_{12}	228	3.09	289	2.84	331	3.17
II	acetone					354	3.19
	$CHCl_3$			313	2.94	356	3.16
	CCl_4			315	2.85	352	2.02
	C_6H_{12}	236	2.97	309	2.50	347	2.97
III	acetone					347	3.26
	$CHCl_3$			302	2.78	349	3.21
	CCl_4			310sh	2.73	350	3.07
	C_6H_{12}	236	3.14	300	2.94	336	3.24
IV	acetone					346	3.12
	$CHCl_3$	258sh	2.84	305	2.94	356	3.09
	CCl_4			300	2.99	358	3.17
	C_6H_{12}	267	2.72	297	2.81	346	3.03
V	acetone					346	3.24
	$CHCl_3$			305	2.74	356	3.25
	CCl_4			307	2.88	348	3.22
	C_6H_{12}	239	3.04	305	2.85	342	3.12
VI	acetone					353	3.42
	$CHCl_3$			300	2.62	355	3.17
VII	acetone					372	3.49
	$CHCl_3$			290	2.68	370	3.46
VIII	acetone					425	3.60
	$CHCl_3$			320	3.52	424	3.38
X	acetone					355	3.33
	$CHCl_3$			280	2.98	346	3.49
	CCl_4					339	3.13

C_6H_{12}: cyclohexane, sh: shoulder

Spectra in Buffer Solutions.

The visible absorption spectra of the compounds under investigation in universal buffer solutions (Fig. 4) exhibit two bands. The spectra at low pH values are comparable to those observed in organic solvents and are mainly due to absorption by the species with nonionized OH-group. On increasing the pH of the medium, the ionization of the proton starts which increases the proportion of the ionic form in solution. It also enhances the intramolecular charge transfer leading to an easier excitation of the π-electrons on the N=N center. The spectra of the-

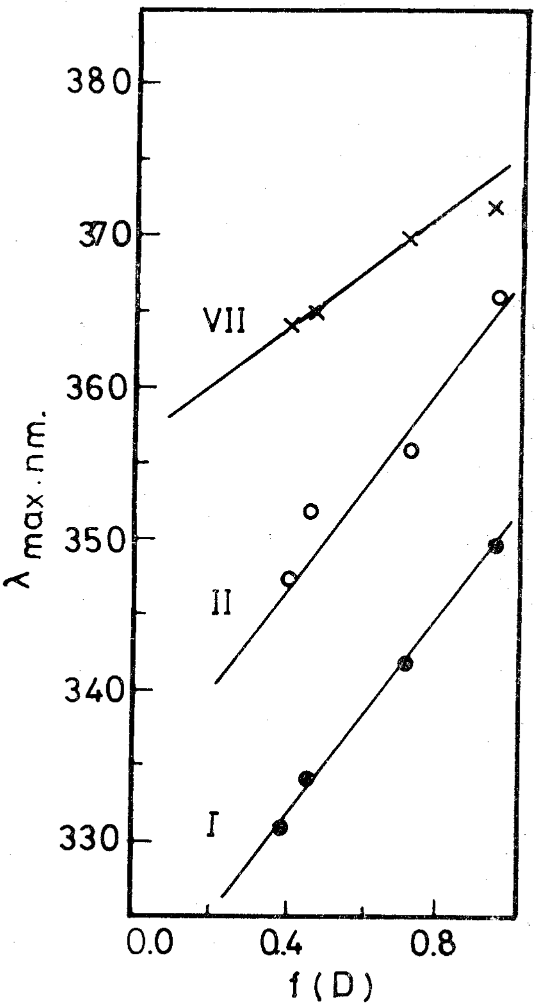


Fig. (3). Relation between λ_{max} nm and f (D).

se compounds in aqueous solutions support the presence of the keto-enol tautomerism. The absorption spectra show a clear isosbestic point indicating the existence of an equilibrium set between the ionized and non-ionized species in solutions. The absorbance-pH curves are typical dissociation or association curves. The dissociation constant of the acid base equilibrium is determined applying the methods considered previously i.e. the half height, the limiting absorbance and the Colleter methods[12,13]. The results are depicted in Table (4). These results indicate

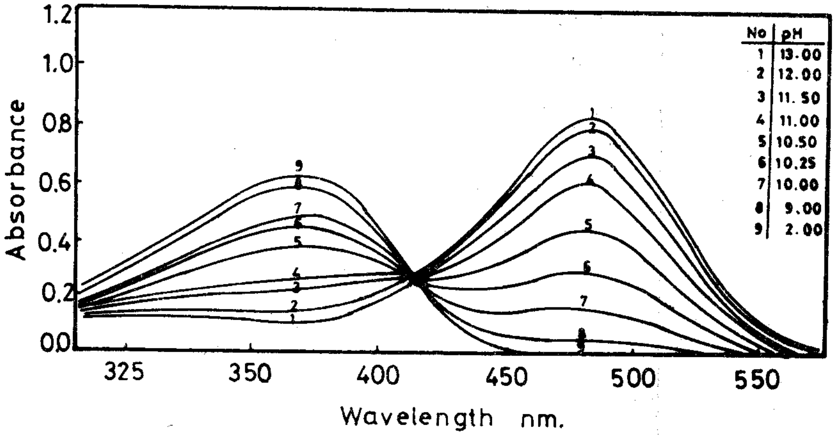


Fig. (4). Absorption spectra of 1-(0,p-dinitrophenylazo)-propane-2-one in buffer solutions of varying pH values.

Table 4. Cumulative data obtained in buffer solutions.

No.	x	non ionic		ionic form		pKa value				$-\Delta G^\circ$
		λ_{max}	$\log\varepsilon$	λ_{max}	$\log\varepsilon$	1	2	3	mean	
I	H	360	4.40	404	4.42	11.38	11.25	11.20	11.27	15.61
II	p-OCH_3	365	4.38	405	4.30	11.63	11.60	11.55	11.59	16.05
III	p-CH_3	360	4.32	400	4.33	11.90	11.95	11.80	11.88	16.45
IV	p-Cl	448	4.40	460	4.36	11.35	11.40	11.30	11.35	15.72
V	p-Br	358	4.33	400	4.38	11.25	11.15	11.15	11.18	15.48
VI	p-COOH	365	4.45	418	4.40	11.75	11.65	11.70	11.73	16.24
VII	p-NO_2	390	4.56	494	4.61	11.20	11.20	11.00	11.13	15.41
VIII	m-NO_2	425	4.24	450	4.42	11.03	10.81	10.75	10.86	15.04
IX	o-NO_2	320	4.45	390	4.61	11.23	11.10	11.00	11.11	15.38
X	o,p-NO_2	370	4.31	483	4.44	10.70	10.65	10.60	10.65	14.75

1: Half height method, 2: Limiting logarithmic method 3: Colleter method
λ_{max} : nm, ΔG° Kcal / mole

that the pK value is dependent on the nature of the substituent (x). Compounds containing nitro group have lower pK values indicating increased acidity of the OH-group. The plot of the pK values as a function of the Hammett substituent constant (σ) is a straight line, the equation of which is

$$pKx = 11.52 - 0.63\ \sigma$$

The negative slope of the straight line indicates that the substituents exert their action in the normal manner.

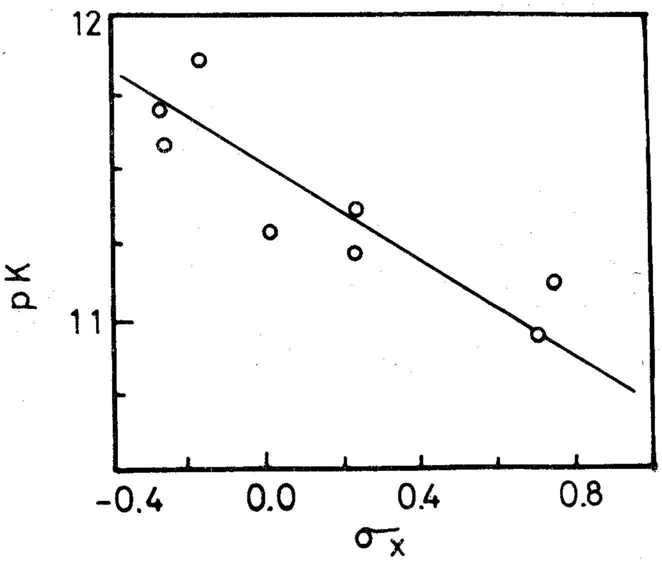


Fig. (5). Dependence of pK values ofn the Hammett substituent effect (σ_x).

REFERENCES

1- JAFFE, H.H., SI-JUNG YEH AND GORDER, R.W., J. Mol. Spectroscopy, 2, 120 (1958).

2- KORNER, I. AND BOCK, G., Chem. Ber., 101, 1922 (1968).

3- ISSA, I.M., ISSA, R.M., MAHMOUD, M.R. AND TEMERIK, Y.M., Z. Physik. Chem., 253, 289 (1973).

4- PANO, G., Kis. Compt., 245, 1145 (1957).

5- RAO, C.N.R., "Chemical Applications of Infrared spectroscopy" Academic Press (London) (1963).

6- EAIW, S.H., ISSA, Y.M. AND ISSA, F.M., Egypt. J. Chem., 20, 545. (1977).

7- NINEHAM, A.W., Chem. Revs., 55, 355 (1955).

8- VOGEL, A.I., "Practical Organic Chemistry", Longmans (london) 3rd Ed. (1963).

9- BRITTON, H.T.S., "Hydrogen Ions" Vol. 1, 2 nd Ed. Chapman and Hall (london) (1952).

10- UENO, K., J. Am. Chem. Soc., 79, 3205 (1957).

11- GATI, L. AND SZALAY, L., Acta Phys. et Chim., 5, 87 (1950).

12- ISSA, R.M. AND ZEWAIL, A.H., J. Chem. UAR, 14, 461 (1971).

13- COLLETER, J.C., Ann. Chim., 5, 415 (1950).