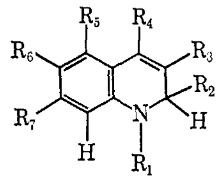
Table I



Compound no.	R_1	R_2	R_3	R_4	R_5	R_6	R_7	Colored form in EPA matrix at 77°K
1	COC_6H_5	CN	H	H	H	H	H	Brownish red
2	$CO_2C_2H_5$	CN	H	H	H	H	H	Orange
3	$CO_2C_2H_5$	OC_2H_5	H	H	H	H	H	Pink
4	CN	OH	H	H	H	H	H	Blue
5	COC_6H_5	CN	H	H	Benzo		H	Yellow
6	$SO_2C_6H_4CH_3$	H	CN	OCH_3	H	H	OCH_3	None

Compound **3** was subjected to the three irradiation–thermal eradication cycles. The total reversibility after the three cycles was better than 99% as determined by monitoring the absorption of the uncolored form in the region 280–310 nm. Similarly, compounds **1** and **5** were cycled five times with the complete disappearance of the visible band after each cycle. Reversibility was 97–98% per cycle. In the cases the of compounds **1** and **5**, there is some side reaction in addition to the reversible photochromic process. This is responsible for the gradual development of an additional band with an onset in the 370–400-nm region. The reversibility of compounds **2** and **4** was considerably lower than those considered above.

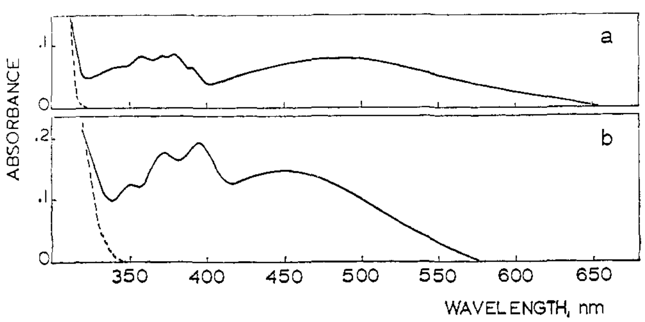
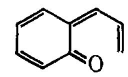


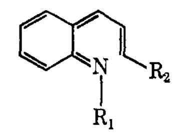
Figure 1. Absorption spectra of colored forms (——) of: (a) 1-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (1.2×10^{-3} *M* at 20° in EPA); (b) 1-benzoyl-2-cyano-1,2-dihydroquinoline (5.7×10^{-4} *M* at 20° in EPA). All spectra were taken in 2-mm Suprasil cells at −196°, irradiated 20 min with 1-kW Hg-Xe source at −196°; colorless forms before irradiation, - - - -.

The colored forms of dihydroquinolines **2** and **5** persist upon melting of the EPA matrix and warming up to room temperature, at which temperature they stay for some time. Some of the compounds (*e.g.*, **1**, **2**, and **5**) can be converted to their colored forms in liquid solution at −75°, and compound **2** at temperatures above 0°. Photochromism of the 1,2-dihydroquinolines seems to depend strongly upon the presence and nature of the substituents in positions 1 and 2; see Table I. Thus, compound **6** is not convertible to a colored form, and its first absorption band stays virtually unchanged upon prolonged irradiation. This effect of substituents is being studied further.

Absorption spectra of the colored forms of all compounds investigated show a broad band in the visible region and a more intense, usually structured band in the region 320–400 nm. Examples are given in Figure 1. A striking similarity exists with the absorption spectra of the colored forms of chromenes;[4] we have shown the structure of the colored form[5] to be **7**. This



7



8

indicates the strong possibility of a parallel structure **8** for the colored form of the 1,2-dihydroquinolines. A more detailed investigation of the photochemistry and spectroscopy of the dihydroquinolines is in progress.

Acknowledgment. This research was supported by the National Aeronautics and Space Administration, Grant NGR 44-005-091.

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Jaroslav Kolc, Ralph S. Becker
Department of Chemistry, University of Houston
Houston, Texas 77004
Received July 17, 1969

Solvent Effects on Molecular Complex Formation. Pyridine–Iodine System

Sir:

Recently, results were presented showing the influence of nonpolar solvents on the pyridine–iodine complex formation reaction.[1] The variation of the 1:1 complex formation constant (K_c, in liters/mole units) was related to the solubility parameters of the solvents (δ_s) by the expression proposed by Buchowski, *et al.*[2]

$$\log K_c = a + b\delta_s \qquad (1)$$

in which a and b are parameters depending only on the properties of the donor (D) and acceptor (A). An alternative method has also been developed for predicting the effect of solvation on complex formation

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equilibria;[3-6] one useful relation which can be derived is

$$\log K_c^s = \log K_c^{ref} + (\alpha - 1)\log(K_{D,A}K_{D,D}) \quad (2)$$

in which K_c^s and K_c^{ref} represent 1:1 formation constants for the reaction in solvent s and in a reference medium (either another solvent or the vapor phase), respectively; α represents the ratio of the free energy of transfer of the complex (from the reference medium into solvent s) to the sum of the free energies of transfer of the uncomplexed donor and acceptor; and $K_{D,A}$ and $K_{D,D}$ are distribution ratios at infinite dilution for the solutes A and D, respectively, between solvent s and the reference medium. ($K_{D,A}$, for example, may be equated to the ratio of the limiting Henry's law constant of A in the reference medium, in units of pressure/molarity, to that of A in solvent s.) Although eq 1 utilizes the solubility parameters of the solvents, eq 2 requires values of the relative solubilities of donor and acceptor in the solvents. According to regular solution theory, solubilities of a solute may be predicted from a knowledge of partial molar volumes and solubility parameters of the solute and solvents.[7] Therefore, the two methods for correlating solvent effects should be closely related, at least as applied to donor–acceptor equilibria occurring in regular solutions. The purpose of the present communication is to show the connection between the methods and to compare their utility in treating data for the pyridine–iodine system.

If a solute (i) dissolves in solvent s to form a regular solution, the rational activity coefficient of i at infinite dilution is given by

$$\gamma_i^s = \exp[\bar{V}_i^s(\delta_i - \delta_s)^2/RT] \quad (3)$$

in which $\bar{V}_i^s$ is the partial molar volume of i at infinite dilution in s and δ_i is the solubility parameter of i.[7] The distribution constant for i between s and the reference solvent may be calculated by substituting values for γ_i^s and γ_i^{ref}, determined using eq 3, into the expression

$$K_{D,i} = \gamma_i^{ref}\bar{V}_{ref}/(\gamma_i^s\bar{V}_s)$$

to obtain

$$K_{D,i} = (\bar{V}_{ref}/\bar{V}_s)\exp\left[\frac{\bar{V}_i^{ref}}{RT}(\delta_i - \delta_{ref})^2 - \frac{\bar{V}_i^s}{RT}(\delta_i - \delta_s)^2\right] \quad (4)$$

in which $\bar{V}_{ref}$ and δ_{ref} are the molar volume and solubility parameter of the reference solvent and $\bar{V}_s$ is the molar volume of s. Substitution of eq 4 for D and A into relation 2 yields

$$\log K_c^s = \log K_c^{ref} + \left[\frac{\bar{V}_A^{ref}}{2.3RT}(\delta_A - \delta_{ref})^2 - \frac{\bar{V}_A^s}{2.3RT}(\delta_A - \delta_s)^2 + \frac{\bar{V}_D^{ref}}{2.3RT}(\delta_D - \delta_{ref})^2 - \frac{\bar{V}_D^s}{2.3RT}(\delta_D - \delta_s)^2 + 2\log(\bar{V}_{ref}/\bar{V}_s)\right](\alpha - 1)$$

or

$$\log K_c^s = \log K_c^{ref} + (\alpha - 1)X \quad (5)$$

in which the function X may be computed from values of the solubility parameters and partial molar volumes of the solutes A and D, solvent s, and the reference solvent. By definition, X equals zero for the reference solvent. Although several variables contribute to X, it is obvious that eq 5 and 1 are quite similar, since only δ_s and $\bar{V}_s$ in (5) vary significantly with choice of solvent.

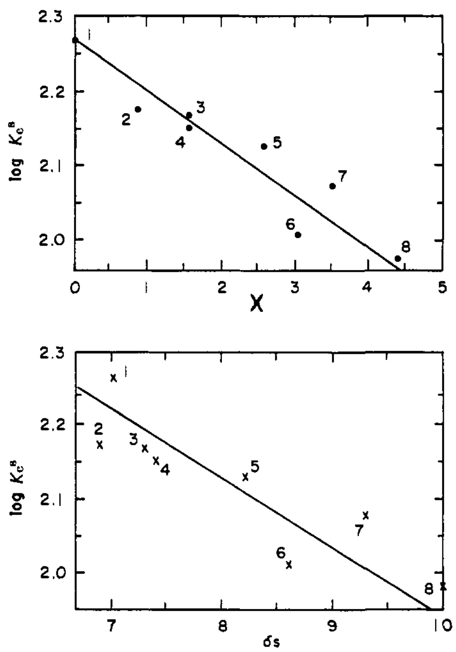

Figure 1. Correlation of log K_c^s with X and with δ_s. Lines are calculated by linear least-squares analysis; points represent data from ref 1 for solvents: squalane (1); isooctane (2); *n*-hexane (3); *n*-heptane (4); cyclohexane (5); CCl_4 (6); C_2Cl_4 (7); CS_2 (8). Root-mean-square deviation of log K_c^s equals 0.033 for upper plot, 0.050 for lower plot.

Figure 1 shows a plot of log K_c^s *vs.* X for the iodine–pyridine reaction in several solvents, using data from ref 1, values of $\bar{V}_D$ calculated from eq 8.10 of ref 7, $\bar{V}_A$ values taken from Table 9.1 of ref 7 or estimated for similar solvents, and $\bar{V}$ = 520 cm³/mole for squalane (2,6,10,15,19,23-hexamethyltetracosane). Because of its relative inertness, squalane has been chosen as the reference solvent. The data are well correlated with the linear relation implied by eq 5, assuming α to be constant; the straight line drawn in the figure has a slope equal to -0.07, from which the value $\alpha = 0.93$ may be calculated. Included in the figure are data from ref 1, plotted in the form log K_c^s *vs.* δ_s. The correlation of log K_c^s with X is somewhat better than that with δ_s, primarily because of the good agreement between the measured value of log K_c^s for squalane and the value predicted using eq 5. The improvement reflects the

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importance of the term 2 log ($\bar{V}_{ref}/\bar{V}_s$) in the variable X; no corresponding solvent volume term is included in eq 1.

The value $\alpha = 0.93$ indicates that the free energy of solvation of pyridine·I_2 is only slightly less than the sum of the free energies of solvation of the uncomplexed pyridine and I_2 molecules. Values of α in the range 0.7–0.8 have been calculated for relatively weak 1:1 hydrogen-bonded complexes,[4] whereas the value α = 1.30 has been reported for the strong 1:1 charge-transfer complex between SO_2 and trimethylamine (TMA).[5] It has been proposed that the large dipole moment of TMA·SO_2 (compared to the vector sum of the moments of TMA and SO_2) is responsible for the abnormally large free energy and energy of solvation of the complex and the corresponding large value of α.[5] Apparently dipole enhancement is insufficient in pyridine·I_2 to overcome the loss (in magnitude) of solvation free energy that occurs when the solvated D and A molecules are brought together to form the solvated complex.

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Sherril D. Christian
Department of Chemistry
The University of Oklahoma, Norman, Oklahoma 73069
Received July 28, 1969

Reactions of Carbalkoxycarbenes with Allyl Halides. Halonium Ylide Intermediates

Sir:

We previously reported that with dialkyl sulfides singlet carbalkoxycarbene directly attacks the unshared electrons on the sulfur atom to form alkylsulfonium ylides, but triplet carbalkoxycarbene cannot interact with unshared electrons on the sulfur atom and does not form the ylide.[1,2]

We extended the studies on the reactions of carbenes with unshared electrons to the halides. The reactions of allyl halides with carbenes have been studied by several workers,[3,4] but there seems to be no report on the reaction with carbenes produced by photochemical, especially by photosensitized, reactions.

In this communication we wish to present the direct and photsensitized decomposition of diazocarbonyl compounds in allyl halides. Irradiation of a solution of dimethyl diazomalonate in an allyl halide was carried out in a Pyrex vessel with a high-pressure mercury lamp.[5] The reaction mixture was analyzed by vapor phase chromatography, and the structures of the isolated products were determined by nmr and ir spectra and elemental analysis.

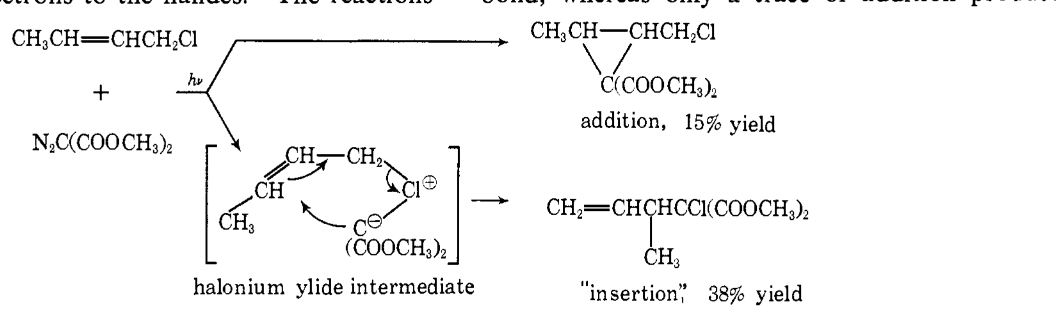
The direct photolysis of dimethyl diazomalonate yields a singlet bis(carbomethoxy)carbene (I) which reacts with allyl chloride to give 53% of allyl chloromalonate and 23% of the cyclopropane derivative.

Table I. The Photolysis of Diazocarbonyl Compounds in Allyl Halides

Diazo compd	Halide	Insertion,[c] %	Addition,[d] %
DM[a]	$CH_2{=}CHCH_2Cl$	53	23
DM	$CH_2{=}C(CH_3)CH_2Cl$	25	22
DM	$CH_3CH{=}CHCH_2Cl$	38[e]	15
DM	$CH_2{=}CHCH_2Br$[h]	38	6
DA[b]	$CH_2{=}CHCH_2Cl$	21	18[f]
DA	$CH_3CH{=}CHCH_2Cl$	15[g]	7[f]

[a] Dimethyl diazomalonate. [b] Ethyl diazoacetate. [c] Allyl halide insertion product. [d] Olefin double bond addition. [e] α-Methylallyl chloromalonate. [f] Mixtures of *cis-* and *trans*-cyclopropanes. [g] Mixtures of α- and γ-methylallyl chloroethylacetate. [h] 37% of dimethyl bromomalonate was also obtained. Under the reaction conditions, the insertion product was unstable.

With γ-methylallyl chloride the formation of α-methylallyl chloromalonate and the cyclopropane were observed, but no γ-methylallyl chloromalonate was obtained.[6] The formation of "insertion" products may be explained by the formation of halonium ylide followed by intramolecular allylic rearrangement (eq 1), as in the case of the reaction of bis(carbomethoxy)carbene with allyl sulfide or in the rearrangement of allylic sulfonium and ammonium ylides.[2,7–10] With allyl bromide, an excellent yield was obtained by the "insertion" of bis(carbomethoxy)carbene into the carbon–bromine bond, whereas only a trace of addition product was



(1)

formed. In the reaction of bis(carbomethoxy)carbene with *trans*-1,4-dichloro-2-butene, the ratio of "insertion" to addition was about twice that obtained with allyl chloride, as is expected from the number of reactive chlorine atoms in the former substrate.

The most marked change in going from the direct photolysis to the sensitized one is in the ratio of the "in-

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(6) Under the reaction conditions, there was insignificant isomerization of the solvent, and the products were neither isomerized nor destroyed.
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