

*Anal.* Calcd for  $C_9H_{10}OCl_2$ : C, 52.68; H, 4.88. Found: C, 52.50; H, 4.95.

**5,6-Dimethyl-6-dichloromethylcyclohexa-2,4-dienone (VIII).**

—To a well-stirred solution of 100 g of 2,3-dimethylphenol and 200 g of sodium hydroxide in 2000 ml of water was added dropwise 240 g of chloroform over a period of 2 hr. The resulting mixture was allowed to stir without heating for 1 additional hr and was then heated under reflux on a steam bath for 3 hr. After cooling to room temperature, the mixture was extracted with two 250-ml portions of ether. The combined ether extracts were washed with two 100-ml portions of water, four 100-ml portions of 10% sodium hydroxide, three 100-ml portions of water, and dried over anhydrous magnesium sulfate. The 28.3 g of red oil remaining after removal of the solvent ether on a rotary vacuum evaporator was distilled through a 60-cm tantalum spiral column to give 17.0 g (10% yield) of VIII as a light yellow oil: bp 71–73° (0.60 mm),  $n_D^{20}$  1.5509.

*Anal.* Calcd for  $C_9H_{10}OCl_2$ : C, 52.68; H, 4.88. Found: C, 52.89; H, 5.00.

**Registry No.**—I, 6611-78-5; II, 14789-73-2; III, 14789-74-3; IV, 14789-75-4; V, 14789-76-5; VI, 14789-77-6; VII, 14789-78-7; VIII, 14789-79-8.

**Acknowledgment.**—The author is indebted to the University of California, Davis, for receipt of a Faculty Fellowship for the summer of 1966.

**The Effect of Ground-State Solvation on the  $n \rightarrow \pi^*$  Transition of Ethyl Acetate<sup>1a,b</sup>**

W. D. CLOSSON<sup>1c</sup> AND PETER J. ORENSKI<sup>1d</sup>

Department of Chemistry, Columbia University,  
New York, New York 10027

Received July 24, 1967

The availability of partial molal heats of solution ( $\Delta\bar{H}_s$ ) of ethyl acetate in several ethanol–water mixtures<sup>2</sup> made it of interest to compare this ground-state solvation effect with the solvent effect on the  $n \rightarrow \pi^*$  transition of the ester in the same solvents. Formally, as discussed by Arnett and co-workers,<sup>3</sup> one may estimate the solvent effect on the heat of solution of the excited state,  $\delta_M\Delta\bar{H}_s^{EX}$ , by the expression

$$\delta_M\Delta\bar{H}_s^{EX} = \delta_M E_T + \delta_M\Delta\bar{H}_s^g$$

where  $\delta_M E_T$  is the solvent effect on the transition energy and  $\delta_M\Delta\bar{H}_s^g$ , the solvent effect on the heat of solution of the ground state. The  $\Delta\bar{H}_s$  data of Arnett and coworkers<sup>2</sup> and the spectroscopic data for the  $n \rightarrow \pi^*$  transition of ethyl acetate in ethanol–water solutions are presented in Table I. In Table II are presented the solvent-effect data, using pure water as reference solvent. Whereas the  $n \rightarrow \pi^*$  transition of ethyl acetate is, of course, a rather broad (but symmetrical) band, and the value of  $\lambda_{max}$  corresponds only to the most probable transition energy, the great similarity of shape and height (note the  $\lambda_{max}$  values in Table I) of the band from one solvent mixture to another implies that the entire band envelope is being

(1) (a) The Electronic Absorption Spectra of Carboxylate Derivatives. V. For part IV see W. D. Closson, P. J. Orenski, and B. M. Goldschmidt, *J. Org. Chem.*, **32**, 3160 (1967). (b) Supported in part by the National Science Foundation. (c) To whom correspondence should be addressed: Department of Chemistry, State University of New York at Albany, Albany, N. Y. 12203. (d) National Institutes of Health Predoctoral Fellow, 1965–1967.

(2) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).

(3) E. M. Arnett, D. Hufford, and D. R. McKelvey, *ibid.*, **88**, 3142 (1966).

TABLE I  
HEATS OF SOLUTION AND SPECTROSCOPIC DATA FOR  
ETHYL ACETATE IN AQUEOUS ETHANOL

Mole fraction of H <sub>2</sub> O	$\Delta\bar{H}_s^g$	$\lambda_{max}, \text{Å}^b$	$\epsilon_{max}$	$E_T, \text{kcal/mole}$	$Z^c$
1.000	-2.36	2041	58	140.1	94.6
0.929	+0.23	2043	58	139.9	93.4
0.906	1.12	2045	58	139.8	92.9
0.884	1.78	2047	59	139.7	92.5
0.857	2.08	2048	57	139.6	91.7
0.830	2.14	2052	58	139.3	90.8
0.798	1.94	2057	59	139.0	90.2
0.765	1.97	2058	58	138.9	89.3
0.726	1.62	2060	59	138.8	89.7
0.684	1.56	2062	59	138.7	88.0
0.582	1.25	2066	58	138.4	86.6
0.000		2083	59	137.3	79.6

<sup>a</sup> Data from ref 2, in kcal/mole. <sup>b</sup> Precision of measurement is at least  $\pm 3 \text{ Å}$ , corresponding to about 0.2 kcal/mole in transition energy ( $E_T$ ). <sup>c</sup> Values of  $Z$ , the solvent polarity parameter, either are from ref 6c or were calculated from the relationship  $Y = 0.35338Z - 29.946$  and the known  $Y$  values, from ref 11 or A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).

TABLE II  
SOLVENT EFFECTS ON TRANSITION ENERGIES AND HEATS  
OF SOLUTION OF ETHYL ACETATE IN AQUEOUS ETHANOL<sup>a</sup>

Mole fraction of H <sub>2</sub> O	$\delta_M E_T$	$\delta_M\Delta\bar{H}_s^g$	$\delta_M\Delta\bar{H}_s^{EX}$
1.000	0	0	0
0.929	-0.2	2.59	2.4
0.906	-0.3	3.48	3.2
0.884	-0.4	4.14	3.7
0.857	-0.5	4.44	3.9
0.830	-0.8	4.50	3.7
0.798	-1.1	4.30	3.2
0.765	-1.2	4.33	3.1
0.726	-1.3	3.98	2.7
0.684	-1.4	3.92	2.5
0.582	-1.7	3.61	1.9

<sup>a</sup> Calculated from the data in Table I, and relative to pure water solvent. Symbols are explained in text, energies are in kcal/mole.

shifted smoothly, and that it is meaningful to examine the variation of  $E_T$  based on the value of  $\lambda_{max}$ .

On examination of Table II, it can be seen that in solvents of high water content there is little difference in solvent effect on the heats of solution of ground and excited states. Thus, in a region of solvent composition where the ground state goes through rather large changes of energy (note the  $\Delta\bar{H}_s$  values in Table I) the transition energy varies only slightly, continuing its slow, steady increase with increasing water content that it exhibits across the entire solvent composition range. In particular, there is no reversible solvatochromic shift associated with the endothermic maxima of  $\Delta\bar{H}_s^g$  (near 0.85 mole fraction of water) similar to that observed by Arnett and coworkers<sup>3,4</sup> for several aromatic compounds in aqueous *t*-butyl alcohol solvents. While at the low-water end of the solvent range there does appear to be a modest ground-state solvation contribution to the spectral shift, the data suggest that the bulk of the solvent–solute interaction changes very little between ground and excited states in very polar solvents.

Actually, the  $n \rightarrow \pi^*$  transition of carboxylic acid esters is quite sensitive to solvent polarity,<sup>5</sup> the transi-

(4) E. M. Arnett and D. Hufford, *ibid.*, **88**, 3140 (1966).

(5) (a) W. D. Closson and P. Haug, *ibid.*, **88**, 2384 (1964); (b) W. D. Closson, S. F. Brady, and P. J. Orenski, *J. Org. Chem.*, **30**, 4026 (1965).

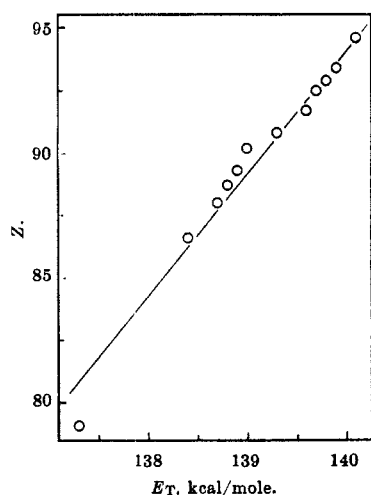


Figure 1.—Plot of ethyl acetate  $n \rightarrow \pi^*$  transition energy ( $E_T$ ) vs. solvent polarity constant ( $Z$ ) in ethanol-water solutions. The least-squares line corresponds to  $E_T = 0.202Z + 121$ ; correlation coefficient = 0.98.

tion energy of ethyl acetate increasing by 4.6 kcal/mole between isooctane and water.<sup>6a</sup> In this respect it is quite similar to the corresponding transitions of many other carbonyl compounds.<sup>6</sup> The similarity of solvent effect on ground- and excited-state heats of solution of ethyl acetate can be interpreted as implying little change in polarity during the  $n \rightarrow \pi^*$  transition, a conclusion in keeping with the known modest decrease of the unsubstituted carbonyl group dipole moment in the  $n, \pi^*$  state.<sup>7</sup> It also suggests that the solvent-solute hydrogen bond, which several lines of evidence indicate is broken during the electronic transition and is not present in the  $n, \pi^*$  excited state of carbonyl compounds,<sup>6a,8</sup> must play only a minor part in determining the total ground-state heat of solution, and presumably, the total excited-state heat of solution. It also suggests that the degree of "structuredness" of the alcohol-water solvent, which frequently has such a marked effect on  $\Delta\bar{H}_s$  values<sup>2,3,9</sup> has a much smaller effect on more intimate types of intermolecular interactions such as hydrogen bonding between a basic center in a molecule and one solvent molecule. On the other hand, the excellent correlation of the  $n \rightarrow \pi^*$  transition energy of ethyl acetate with  $Z^{10}$  and  $Y^{11}$  empirical solvent polarity parameters (note Table I and Figure 1), indicates that these are good measures of solvent hydrogen-bonding ability.

#### Experimental Section

Solvents were prepared by mixing appropriate quantities, measured by volume at 25°, of absolute ethanol and distilled water. Reagent grade ethyl acetate was carefully distilled prior to use. The details of measurement of the ester absorption spectra have been described previously.<sup>6a</sup>

**Registry No.**—Ethyl acetate, 141-78-6.

(6) (a) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 186-188; (b) J. W. Sidman, *Chem. Rev.*, **53**, 689 (1958); (c) E. M. Kosower and G.-S. Wu, *J. Am. Chem. Soc.*, **83**, 3142 (1961).

(7) G. Berthier and J. Serre, "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, p 49.

(8) M. Ito, K. Inuzuka, and S. Imanishi, *J. Chem. Phys.*, **31**, 1694 (1959).

(9) E. M. Arnett and D. R. McKelvey, *J. Am. Chem. Soc.*, **87**, 1393 (1965).

(10) E. M. Kosower, *ibid.*, **80**, 3253, 3261 (1958).

(11) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); J. E. Leffer and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 297-312.

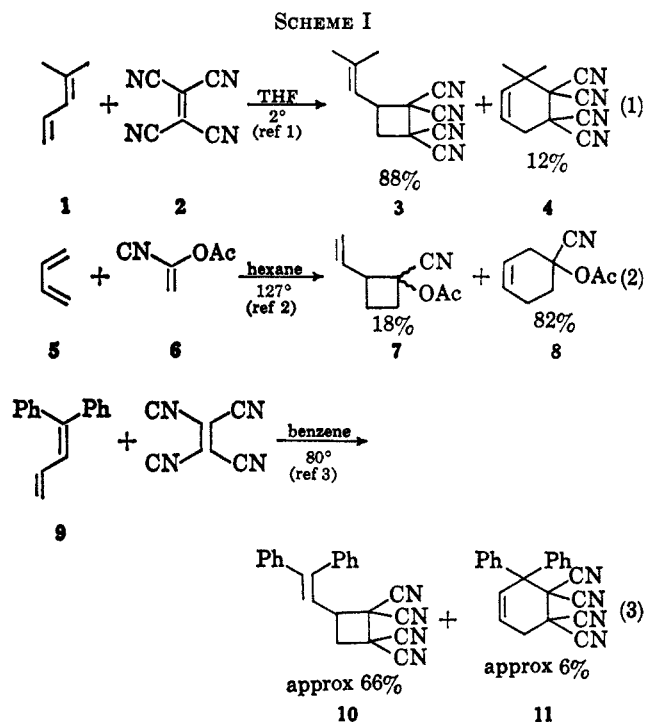
## A Perturbational Molecular Orbital Method Applied to Competing 1,2- and 1,4-Cycloaddition Reactions

WILLIAM C. HERNDON AND JEROLD FEUER

Department of Chemistry, Texas Technological College, Lubbock, Texas 79409

Received May 26, 1967

Three papers have recently appeared which describe Diels-Alder reactions under mild conditions that yield a cyclobutyl derivative in addition to the normal six-membered ring adduct.<sup>1-5</sup> Typical conditions and yields are outlined below. An important fact which attracts an attempt at a theoretical explanation is the drastic change in the relative yields of the two types of products with differing reactants (Scheme I).



The commonly accepted mechanism for cyclobutane formation postulates a diradical intermediate.<sup>6</sup> This diradical is also the most easily visualized intermediate for the reported isomerizations,  $7 \rightarrow 8^8$  and  $10 \rightarrow 11^7$ . Therefore a suggested two-step mechanism involving a diradical intermediate, which can lead to either of the two products,<sup>2</sup> seems reasonable for these reactions.

(1) C. A. Stewart, Jr., *J. Am. Chem. Soc.*, **84**, 117 (1962).

(2) J. C. Little, *ibid.*, **87**, 4020 (1965).

(3) J. J. Eisch and G. R. Husk, *J. Org. Chem.*, **31**, 589 (1966).

(4) Two other examples are the reactions of tetrafluoroethylene with cyclopentadiene [J. J. Drysdale, W. W. Gilbert, H. K. Sinclair, and W. H. Sharkey, *J. Am. Chem. Soc.*, **80**, 245, 3672 (1958)] and the thermal dimerization of butadiene under unusual conditions [H. W. B. Reed, *J. Chem. Soc.*, 685 (1951)]. Schueller has also reported a very small amount of vinylcyclobutane from the reaction of butadiene and ethylene (see ref 5, pp 71-75).

(5) K. E. Schueller, "Cycloaddition Reactions of Ethylene and  $\alpha$ -Acetoxyacrylonitrile," Harvard University Press, Cambridge, Mass., 1966, p 29.

(6) J. D. Roberts and C. M. Shorts, *Org. Reactions*, **12**, 1 (1962); R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 779-791.

(7) M. J. Mintz and J. C. Little, Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, O-154.