The pK_a values thus determined show remarkable strengths for the cyanocarbon acids. Pentacyanopropene and the first ionization of hexacyanoisobutylene are comparable with the stronger mineral acids. Hydrochloric acid, for example, is thought to have a pK_a in the neighborhood of -7.[7] A high degree of resonance stabilization in the anions (which is not possible in protonated form) appears to be responsible for the high acidity.[1]

Smoothed values of the acidity function H_- calculated according to

$$H_- = pKa + \log C_A{}^-/C_{HA}$$

are listed in Table II along with values of H_0 for comparison.[2] The H^- function presented here is based entirely on p-(tricyanovinyl)-phenyldicyanomethane, methyl dicyanoacetate and bis-(tricyanovinyl)-amine.

H_- behaves in a manner surprisingly similar to H_0 although there are quantitative differences. At lower concentrations (<5 M) these appear to be of the kind expected on the basis of the differences in charge types. At higher concentrations H_- roughly parallels H_0. The similarity of these two acidity functions is further evidence that these indicator acidity functions depend primarily on the properties of the hydrogen ion in solution relatively unencumbered by activity coefficient effects of the indicators themselves.[7]

(7) R. P. Bell, "The Proton in Chemistry," Chaps. VI, VII, Cornell University Press, Ithaca, N. Y., 1959.

CONTRIBUTION No. 714
CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION   RICHARD H. BOYD
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON 98, DELAWARE
RECEIVED AUGUST 29, 1961

DEMONSTRATION OF THE "CAGE" EFFECT

Sir:

In 1934, Franck and Rabinowitch[1] pointed out that collision times of reactive molecules should be much longer in solution than in the gas phase. Further, in solution, after the colliding molecules have diffused apart by a distance small compared to the mean distance between reactive molecules, there remains a finite probability of re-encounter before diffusion to the mean distance. Effectively the solvent holds the reactive molecules together, forming a "cage." A more sophisticated treatment using the theory of random walks has been given by Noyes.[2]

Numerous observations have been explained by invoking the cage effect with varying degrees of certainty. Probably the best is a recent study by Herk, Feld, and Szwarc,[3] in which they reaffirm Szwarc's previous conclusion that in the photolysis of azomethane in liquid isoöctane, ethane is formed chiefly by recombination of methyl radicals inside the solvent cage. This conclusion was inferred from three observations: that the CH_4/N_2 ratio was independent of azomethane concentration,

(1) Franck and Rabinowitch, *Trans. Faraday Soc.*, **30**, 120, 9 (1934).

(2) R. M. Noyes, *J. Chem. Phys.*, **18**, 999 (1950), and the following papers.

(3) Herk, Feld, and Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

that ethane formation could be inhibited effectively by radical scavengers in the gas phase photolysis, but not in the liquid, and that the ratio of $CH_4 + 2 C_2H_6/N_2$ was nearly 2.

We believe that since the cage effect is an important concept in solution kinetics, it is of value to confirm its existence directly and unequivocally. We wish in this paper to report such a confirmation.[4]

We have photolyzed mixtures of azomethane and d_6-azomethane in the gas phase and in isoöctane solution using a procedure essentially similar to that of Herk, Feld, and Szwarc.[3] Azomethane was prepared by oxidation of *sym*-dimethylhydrazine with mercuric oxide, while d_6-azomethane was purchased from Merck of Canada. Both materials were proven to be chemically pure by gas chromatography. The isotopic purity of the d_6-azomethane was checked by mass spectra. 3% $CD_3N_2CD_2H$ and no other impurities were found. The isoöctane was spectroscopic grade, further purified by passing through silica gel. Its purity and the cleanliness of our handling procedure were checked by ultraviolet spectra.

The reaction products were analyzed by mass spectroscopy. The cracking patterns of N_2, CD_3-$NNCD_3$, CH_3NNCH_3, and C_2H_6 were determined for our mass spectrometer, while the cracking patterns of C_2D_6, C_2D_5H, and CD_3CH_3 were kindly provided by Mr. J. Bell of Harvard University.[5] C_2D_6, C_2D_5H, CD_3CH_3, and C_2H_6 were determined from the mass 36, 35, 33, and 27 peaks, respectively. From these peak heights, the remaining peaks in the 36 to 24 range could be predicted within 4%.

In the gas phase photolysis of azomethane one would expect ethane to be formed by random recombination of methyl radical. For such a random process, the ethane is formed in proportions such that $(CH_3CD_3)^2/(C_2H_6)(C_2D_6) = 4$. The observed ratio of parent peak heights is 4.1 ± 0.8.

However in the isoöctane solution photolysis, the mass 33 peak is less than 2% of the 36 peak. This peak can be accounted for satisfactorily by the contributions of isotopic carbon and CD_5H. The authors estimate that if any CD_3CH_3 is formed, it must be less than 0.3% of the total ethane.

(4) We have recently become aware of an unpublished study by Ausloos and co-workers at the National Bureau of Standards, whose results somewhat parallel our results.

(5) J. Bell, private communication.

ESSO RESEARCH & ENGINEERING CO.   RICHARD K. LYON
LINDEN, NEW JERSEY   DONALD H. LEVY
RECEIVED SEPTEMBER 11, 1961

ROTATORY-DISPERSION CHANGES DURING THE THERMAL DENATURATION OF CHYMOTRYPSINOGEN AND CHYMOTRYPSIN

Sir:

The effects of denaturing reagents such as urea in producing drastic unfolding of proteins have become so well known as to direct our attention away from the search for other interpretations of major denaturation reactions. In particular, the large entropy changes associated with reversible thermal denaturations may not be the result of