

Figure 5. Theoretical chemical shifts predicted by a modified CNDO-SCF treatment are plotted against the experimental values for the five-membered nitrogen heterocycles and their charged species. The treatment is modified by taking $\Delta E = f \times 10$ eV. The f values, given in Table III, reflect the effect of nitrogen lone pairs on the average excitation parameter.

The calculated f values indicate that only relatively small changes are noted between compounds, but, because of the relatively large magnitude of the paramagnetic shielding term, these variations can make significant contributions to the chemical shift. An

(25) V. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.*, 60, 248 (1964).

(26) A. Mathias and V. M. S. Gil, *Tetrahedron Letters*, 3163 (1965).

examination of the f values in Table III reveals a consistent set of parameters for the various species. Those compounds with two unprotonated nitrogen lone pair (imidazole and pyrazole anions) have the lowest f values (both 0.970). Imidazole, pyrazole, and pyrrole anion, each with one unprotonated nitrogen atom, have slightly higher f values (0.983, 0.984, and 0.985, respectively) which are intermediate between the 0.970 value and the value of 1.00. The completely protonated species (pyrrole, and imidazole and pyrazole cations) have values 0.999, 0.998, and 0.998, respectively, which for all practical purposes may be considered to be 1.00 indicating the similarity of these compounds with the reference cyclopentadienyl anion. The improved correlation noted in Figure 5 over that of Figure 3 lends merit to the Pople and Santry^{22,23} approach.

Considerable optimism would appear to be justified in the use of carbon-13 chemical shift data as a means of investigating refined features of molecular wave functions. As the carbon-13 chemical shift parameter has been rationalized in terms of changes in the charge density and in the bond orders, it is evident that both of these features may be studied in a theoretical assessment of carbon-13 magnetic resonance data. While there is a temptation to correlate chemical shifts with only charge densities because of recent successes in such studies,^{6,7} protonation data of the type contained herein suggests the need to include bond order effects in future considerations of carbon-13 chemical shifts.

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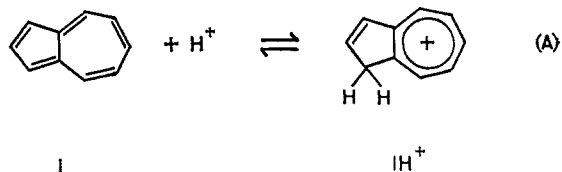
Proton Dissociation of Azulenium Cations in the Excited State

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Abstract: Solutions of many azulenum cations in aqueous sulfuric acid (corresponding to H_0 values below -5 on a Hammett scale) fluoresce strongly. This fluorescence is quenched in less acidic solutions (H_0 between -4 and -1). By means of flash experiments it can be shown that the quenching mechanism involves the proton dissociation of the excited azulenum cation. One of the transients generated is azulene in its ground state, which leads to a distortion of the ground-state equilibrium, azulene \rightleftharpoons azulenum cation. The relaxation time of the distorted equilibrium has been measured as a function of H_0 and compared with the known values obtained by a fast-flow method.

Azulene (I) and its derivatives protonate in strongly acidic media to yield the azulenum cation IH^+ and the corresponding derivatives.² In contrast to the azulenes which fluoresce only weakly at room temperature,^{3a} their conjugate acids exhibit a strong fluores-

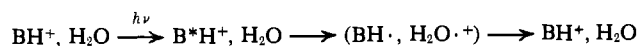


(1) (a) Max-Planck-Institut; (b) Eidg. Technische Hochschule.
(2) P. A. Plattner, E. Heilbronner, and S. Weber, *Helv. Chim. Acta*, 35, 1036 (1952); F. A. Long and J. Schulze, *J. Am. Chem. Soc.*, 83, 3340 (1961).

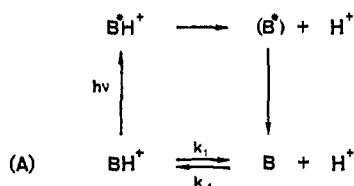
(3) (a) M. Beer and H. C. Longuet-Higgins, *J. Chem. Phys.*, 23, 1390

(1955); G. Viswanath and M. Kasha, *ibid.*, 24, 574 (1956); G. Binsch, E. Heilbronner, R. Jankow, and D. Schmidt, *Chem. Phys. Letters*, 1,

cence when dissolved in a solvent of sufficiently high acidity.^{3b} In a recent study of the dependence of the fluorescence intensity on the proton activity of the solvent, as measured by the Hammett acidity function H_0 , it was proposed that azulenum cations are stronger acids in their electronically excited state than in the ground state.⁴ This fact, which is already suggested by the strong blue shift of the long-wave transition of azulenes on protonation (from 17,000 to 28,000 cm^{-1} in the case of the parent hydrocarbon) has been deduced from the observation that the H_0 value of the solvent (aqueous sulfuric acid) had to be at least four units more negative than the one corresponding to the $\text{p}K'$ value measured for the ground-state equilibrium A, to afford an appreciable fluorescence intensity. However, the dissociation of an electronically excited azulenum cation is not the only possible explanation for the observed fluorescence quenching. By analogy to the behavior of the tropylium cation, one would expect that azulenum cations would be strong electron acceptors⁵ and that their electron affinities would be even greater in the excited state. Even a weak electron donor like water could therefore be responsible for the fluorescence quenching through an electron-transfer mechanism of the following type (where B stands for an unspecified conjugate base, e.g., azulene B = I).



On the other hand, dissociation of the electronically excited cation I^*H^+ (= B^*H^+) would yield either an excited free base molecule I^* (= B^*) which then would undergo internal conversion to the ground state (see diagram) or directly the ground-state free base I (= B) through a sequence of nonspectroscopic states, bypassing I^* . In both cases the dissociation of I^*H^+ will finally lead to the formation of the free base I (= B) in its ground state and hence to a distortion of the ground-state equilibrium A. The relaxation



time $\tau = (k_1 + k_{-1})^{-1}$ of equilibrium A is of the order of milliseconds⁶ and should therefore be easily measurable in a flash-photolysis experiment. (This same method has been applied previously in a study of fast protolytic reactions.⁷)

As will be shown, illumination of solutions of azulenum cations in aqueous sulfuric or perchloric acid ($H_0 = -3$ to -1) with a strong flash causes indeed the postulated shift of the ground-state equilibrium, thus indicating that proton dissociation in the excited state is the major, if not the only, pathway of the fluorescence quenching reaction. In the following we

135 (1967); (b) W. Treibs and M. Scholz, *Z. Physik. Chem. (Leipzig)*, **212**, 118 (1959); W. Meier, Thesis No. 3515, Federal Institute of Technology, Zürich, 1964.

(4) R. Hagen, E. Heilbronner, W. Meier, and P. Seiler, *Helv. Chim. Acta*, **50**, 1523 (1967).

(5) M. Feldman and S. Winstein, *J. Am. Chem. Soc.*, **83**, 3338 (1961).

(6) B. C. Challis and F. A. Long, *ibid.*, **87**, 1196 (1965).

(7) K. Breitschwerdt and A. Weller, *Ber. Bunsenges. Physik. Chem.*, **64**, 395 (1960).

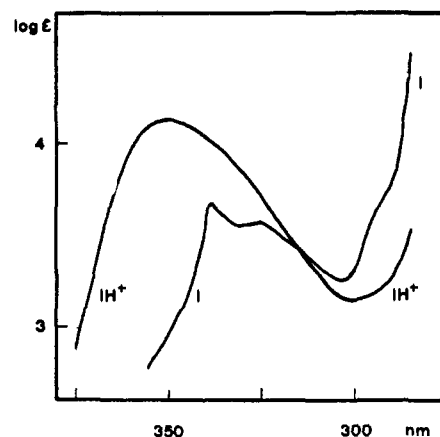
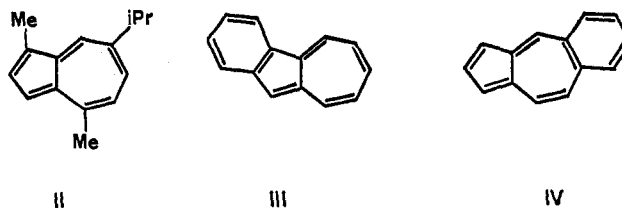


Figure 1. Absorption spectra of azulene (I) in water and of the azulenum cation (IH^+) in aqueous sulfuric acid ($H_0 = -1.82$).

report the results of flash experiments with the conjugate acids of azulene (I), guaiazulene (II), 1,2-benzazulene (III = benz[*a*]azulene), and 5,6-benzazulene (IV = benz[*f*]azulene⁸).



Experimental Section

The exciting light source was a 200-Wsec⁻¹ flash with a half-duration of 5 μsec . The monitoring light was an iodine-quartz lamp whose beam passed through the quartz reaction cell (15-mm i.d., path length 100 mm) and a Bausch & Lomb 250-mm monochromator onto a 1P28 photomultiplier. The photomultiplier signal was recorded with a Tektronix storage oscilloscope, Type 549. The spectra of the transient species were measured with the same setup by changing the wavelength setting of the monochromator in 10-nm steps. In order to exclude errors due to photodecomposition, a fresh solution was used for each wavelength.

The acids used were analytical grade. The hydrocarbons I-IV were either purified commercially available samples (I, II) or samples prepared according to procedures described in the literature (III, IV).⁸

Results and Discussion

The aim of our experiments was to detect the free bases (I-IV) as transients after the exposure of solutions of their conjugate acids (IH^+ - IVH^+) to a strong photoflash. In Figure 1 we show, as an example, the electronic spectra of I and of IH^+ in the spectral range from 375 to 285 nm. From this figure we deduce that the oscilloscope deflections immediately after the flash (*i.e.*, the change in optical density at a given wavelength λ) should be as follows: zero deflection at the wavelength of the isosbestic point (315 nm), an increase in optical density in the region from 285 to 315 nm, and a decrease at longer wavelengths (>315 nm). (The increase in optical density expected in the spectral region around 580 nm, where the free bases absorb and their conjugate acids do not, could be detected. However, these deflections are not

(8) III: P. A. Plattner, A. Fürst, J. Chopin, and G. Winteler, *Helv. Chim. Acta*, **31**, 501 (1948); IV: C. W. Muth, M. L. de Matte, A. R. Urbanik, and W. G. Isner, *J. Org. Chem.*, **31**, 3013 (1966).

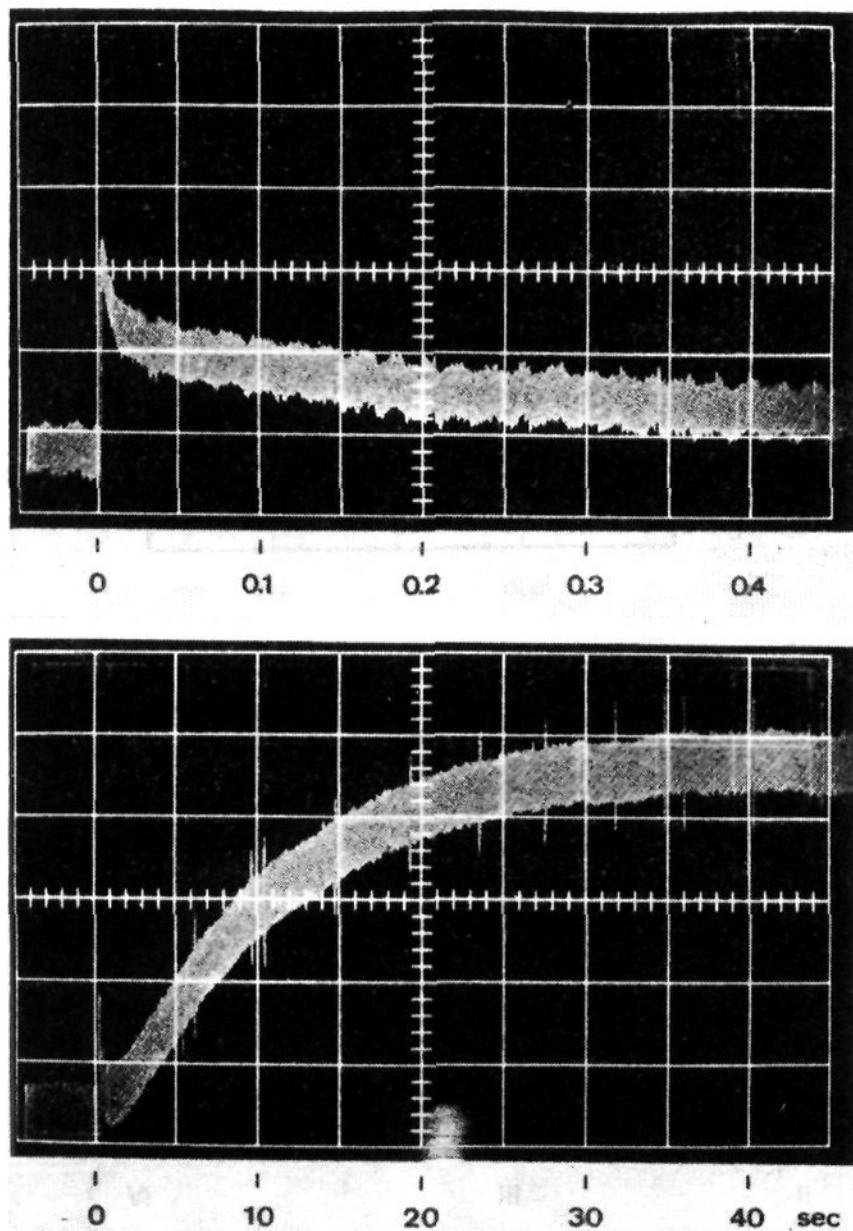


Figure 2. Oscilloscope traces at 580 nm after flashing a 10^{-5} M solution of azulene (I) in aqueous sulfuric acid ($H_0 = -0.03$): time scale, 50 msec/cm (top); 5 sec/cm (bottom).

suitable for precise measurements in view of the low intensity of the long-wave absorption bands of the azulenes.) On the other hand, as the spectrum of the conjugate acid (e.g., IH^+) is known, it is of course possible to calculate from the wavelength dependence of the observed deflections the spectrum of the transient and to compare it to the one we expect, i.e., that of I. Furthermore, from the results reported by Challis and Long,⁶ one would predict that the deflections due to the presence of the free base should go back to zero within a few milliseconds according to first-order kinetics. Both these predictions correspond exactly to what has been observed.

However, before we analyze our results, attention should be drawn to the following two difficulties.

Proton dissociation leading to the free base as a transient is not the only reaction which takes place after photoexcitation, especially when the acidity of the solvent is low. This is shown in Figure 2, where the oscilloscope tracings recorded at a wavelength of 580 nm and with time-scale expansions differing by a factor of 10^2 are presented for a 10^{-5} M solution of I in sulfuric acid with $H_0 = -0.03$. Within the duration of the flash there is a rapid increase in optical density corresponding to the formation of some intermediate(s), which decays in a complicated fashion within 0.4 sec to almost the original value but increases again at a much lower rate within about 30 sec. To avoid these side

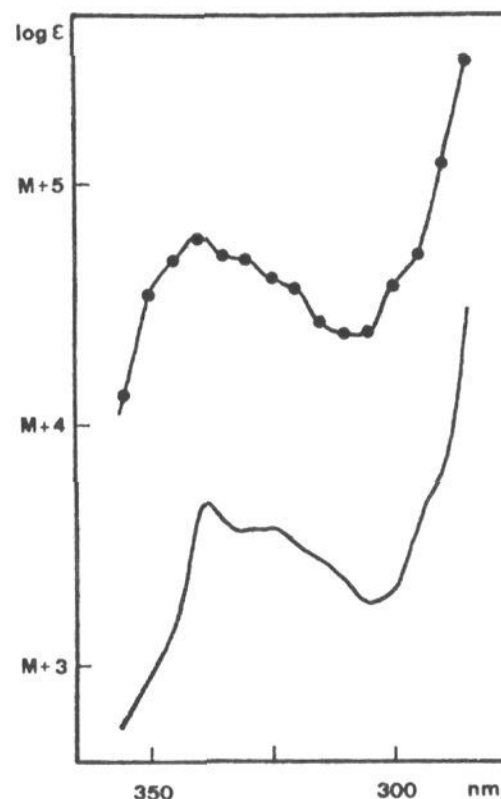


Figure 3. Absorption spectrum of azulene (I) in water (lower curve), $M = 0$, and from flash-photolysis experiments in aqueous sulfuric acid ($H_0 = -1.82$), when a conversion of 8% is assumed (upper curve), $M = -1$.

reactions, which have not yet been analyzed, it has been necessary to work at acidities below $H_0 \approx -1.2$.

On the other hand, reprotonation of the free base becomes extremely fast below $H_0 \approx -2.8$ and exceeds the time resolution of the flash apparatus used in the present experiments, so that our investigations had to be limited to the range of H_0 from -1.2 to -2.8 . The optimum value for the observation of I as a transient lies in the vicinity of $H_0 = -1.8$.

The absorption spectrum of the transient (taking azulene as an example) was determined in the following way: the oscilloscope trace yields as a function of time a photomultiplier signal $V = V(t)$, which is proportional to the transmitted light intensity $i = i(t)$. The signal before the flash is V_0 proportional to i_0 . Therefore

$$\log \frac{V_0}{V(t)} = \log \frac{i_0}{i(t)} = \Delta E(t)$$

$\Delta E(t)$ is the optical density due to the transient, which is again a function of time. The decay of this transient is kinetically of first order and a plot of $\ln \Delta E(t)$ vs. t gives, therefore, a straight line with slope τ^{-1} and intercept $\ln \Delta E(0)$. In this way the values of $\Delta E(0)$ were determined as a function of wavelength (in 10-nm steps). These values yield the electronic spectrum of the transient shown in Figure 3.

In order to convert the $\Delta E(0)$ values into the absorption spectrum of the transient, one must know what per cent of the cation is converted per flash. This conversion factor can only be estimated from measurements at wavelengths where either the cation or the neutral species does not absorb, e.g., at 360 nm. Assuming a conversion factor of 8%, one obtains the spectrum given in Figure 3 which agrees fairly well with an authentic azulene spectrum. Of course, one has to keep in mind that the absorption spectrum of free azulene in sulfuric acid of $H_0 = -1.82$ might be some-

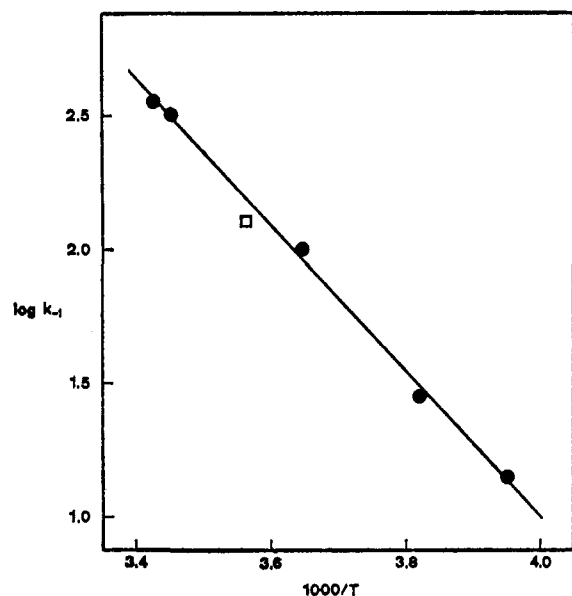


Figure 4. Arrhenius plot of the protonation rate k_{-1} of azulene (I) in 3.65 M perchloric acid: ●, this work; □, ref 6.

what different from that recorded in neutral media by conventional methods.

The rate constants for the decay of the transient obtained from the tracings recorded at different wavelengths agree within $\pm 10\%$. Their dependence on the proton activity of the medium is shown in Table I.

Table I. Relaxation Constant $\tau^{-1} = k_1 + k_{-1}$ of Azulene (I) in Aqueous Sulfuric Acid

H_0	$\tau^{-1} \times 10^{-3}, \text{sec}^{-1}$	
	290 nm	350 nm
-1.50	0.6	0.6
-1.82	1.2	1.3
-2.10	2.3	2.4
-2.39	3.2	...
-2.72	5.9	...

As the deprotonation reaction (k_1) can be neglected at H_0 values more negative than -1.8 , one finds that $\tau^{-1} \approx k_{-1}$. (Only the value at $H_0 = -1.50$ of Table I has to be corrected for the dissociation reaction, which can be done on the basis of the data obtained by Challis and Long.⁶) Under these conditions the values given in Table I fit the equation

$$\log k_{-1} \approx \log \tau^{-1} = (1.45 \pm 0.3) - (0.90 \pm 0.15)H_0$$

The great similarity between the transient spectrum and the normal azulene spectrum (see Figure 3) strongly suggests that proton dissociation takes place in the excited state. This assumption is further supported by the fact that the rate constant k_{-1} measured in the flash experiments, agrees very well with that determined by a completely different method. Challis and Long⁶ have measured the relaxation time of azulene in 1.46 to 3.91 M perchloric acid ($H_0 = -0.510$ to -1.67) at 7.3° with a fast-flow apparatus. In order to compare their rate constants with our flash data we measured k_{-1} in 3.65 M perchloric acid ($H_0 = -1.54$) at different

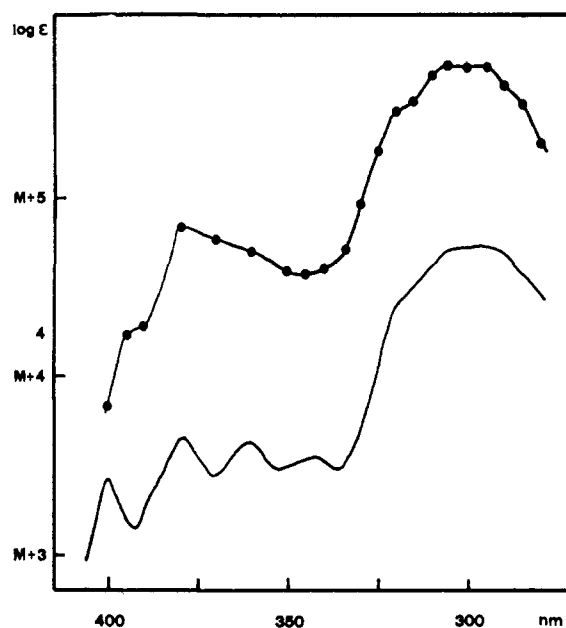


Figure 5. Absorption spectrum of 1,2-benzazulene (III) in 2% ethanol-water (lower curve), $M = 0$, and from flash-photolysis experiments in aqueous sulfuric acid ($H_0 = -1.06$), when a conversion of 60% is assumed (upper curve), $M = -1$.

temperatures. The result is summarized in the Arrhenius plot of Figure 4. Further data obtained by Challis and Long cannot be compared with our results, because the flash method is limited to measurements at more negative H_0 values, whereas the flow method seems to be confined to less acidic solutions.

The conjugate acid IIIH^+ of 1,2-benzazulene (III) shows a similar photochemical behavior to that of azulene. However, the spectrum of the transient can be determined more accurately because in this case the conversion to the free base is approximately 60%. This conversion factor can be obtained quite accurately because the cation absorbs very weakly at 300 nm, where the absorption of the neutral species has a maximum. The calculated spectrum of the transient is given in Figure 5 where it is compared to the electronic spectrum of III.

Table II shows the rate constants τ^{-1} determined as above as a function of the acidity of the solvent. The data in Table II fit the equation $\log k_{-1} \approx \log \tau^{-1} = (1.70 + 0.09) - (1.00 \pm 0.08)H_0$.⁹

Table II. Relaxation Constant $\tau^{-1} = k_1 + k_{-1}$ of 1,2-Benzazulene (III) in Aqueous Sulfuric Acid (Measured at 310 nm)

H_0	$\tau^{-1} \times 10^{-3} \text{sec}^{-1}$
-0.32	0.11
-0.75	0.30
-1.06	0.55
-1.17	0.68
-1.80	3.40

It is tempting to assume that the longer lifetime of the excited state of 1,2-benzazulenium cation (IIIH^+) relative to that of IH^+ , as shown by the fluorescence

(9) The $\text{p}K'$ value of 1,2-benzazulene is $+0.65$. The deprotonation reaction k_1 can therefore be neglected at the H_0 values of Table II.

quantum yields $\varphi(\text{IIIH}^+) \approx 30\varphi(\text{IH}^+)$, is the reason for the high conversion rate of 60%. However, 5,6-benzazulenium cation (IVH^+) fluoresces as strongly as IIIH^+ while only 15% of it is converted to the free base IV after the flash. Presumably differing quantum yields of side reactions and differing rates of the deprotonation reaction in the excited state determine also the conversion rates.

Both 5,6-benzazulene (IV) and guaiazulene (II) have only been investigated qualitatively. The change

in optical density due to one of the transients agrees again with the corresponding absorption spectra of the free hydrocarbons IV and II. However, side reactions are much more predominant. Therefore, the calculation of accurate rate constants was not possible.

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The Primary Salt Effect on Rate of Reaction between Likely Charged Ionic Species by Polyelectrolytes

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Contribution from the Department of Polymer Chemistry, Kyoto University, Kyoto, Japan. Received February 20, 1968

Abstract: The rate constants were measured in the presence of various polyelectrolytes for the following two types of reactions between likely charged ionic species, namely bromoacetate-thiosulfate ion reaction and bromopentaamminecobaltic ion-mercuric ion reaction. Cationic polyelectrolytes such as polyethylenimine hydrochloride considerably enhanced the anion-anion reaction, whereas polystyrenesulfonate and other anionic polyelectrolytes also showed large accelerating effects on the cation-cation reaction. This primary salt effect by polyelectrolytes was markedly larger than that by simple electrolytes and was shown to be due to a lowering of the enthalpy and entropy of activation in contrast to the simple electrolyte cases in which these thermodynamic quantities were increased. The entropy loss by the addition of polyelectrolytes was in conformity to the enhanced regularity of ionic distribution in the polyelectrolyte solutions, which was previously concluded from the mean activity coefficient measurements.

We know that high molecular weight compounds exhibit various characteristic properties, which are not encountered for those of low molecular weight. Catalytic efficiency is not an exception. In this laboratory for example, intensive studies were carried out on the catalytic actions of various types of polysulfonic acids mainly in hydrolysis reactions.¹ The results showed that the reactions could be enhanced considerably more by polymer catalysts than by low molecular weight ones. It was concluded that the rate enhancement was due to nonspecific hydrophobic and electrostatic interactions which gave rise to an abnormally high accumulation of reactant molecules and ions around macroions. Though these investigations covered important aspects of the problem, there is still something to be further explored: no work was published on the catalytic influence of polyelectrolytes on reactions between rather simple ionic species.² The previous studies mentioned above indicate that this type of reaction might also be influenced by polyelectrolytes.

In previous papers from this laboratory, the mean activity coefficients of polyelectrolytes³ were determined

(1) I. Sakurada, Y. Sakaguchi, *et al.*, *Kobunshi Kagaku*, **22**, 696, 701, 706, 711, 804, 808 (1965); **23**, 735, 741, 748, 849, 853 (1966); **24**, 87, 341, 570, 618 (1967); *Makromol. Chem.*, **91**, 243 (1966). For a comprehensive review, see the plenary lecture by I. Sakurada at the International Symposium on Macromolecular Chemistry, 1967, Brussels; *J. Pure Appl. Chem.*, in press.

(2) The catalytic actions of polyelectrolytes on a few reactions between fairly complicated ionic species have been studied; see H. Morawetz, "Macromolecules in Solution," Interscience Publishers, New York, N. Y., 1965, Chapter 9. See also NOTE ADDED IN PROOF.

by emf measurements of a concentration cell with transference⁴ and isopiestic vapor pressure measurements.⁵ The results have revealed that the mean activity coefficients decrease linearly with the cube root of concentration, suggesting the existence of an interionic linkage in the polyelectrolyte solutions. Such thermodynamic behavior was not, however, newly found, but had earlier been pointed out for simple electrolyte solutions.⁶ Nonetheless, it is important to point out that the cube-root rule holds in a much wider range of concentration for polyelectrolytes than for simple electrolytes. For example, the rule is valid between 10^{-3} and 10^{-1} M for sodium chloride, whereas the upper limit lies at about 1 equiv/1000 g of water for sodium polyacrylate.⁷ Since the cube-root relation can be attributed to a more or less regular ionic lattice in the solutions,⁶ it is feasible that strong electrostatic attractive forces between macroions and gegenions give rise to linkages between macroions and between gegenions through the intermediary of gegenions and macroions, respectively. Accordingly, the regular ionic

(3) The mean activity coefficients should be correctly distinguished from the single-ion activity coefficients having no sound physical basis. For related problems peculiar to the polyelectrolyte solutions, see N. Ise and T. Okubo, *J. Phys. Chem.*, **70**, 3025 (1966).

(4) See, for example, N. Ise and T. Okubo, *ibid.*, **69**, 4102 (1965).

(5) See, for example, T. Okubo, N. Ise, and F. Matsui, *J. Amer. Chem. Soc.*, **89**, 3697 (1967).

(6) N. Bjerrum, *Z. Anorg. Chem.*, **109**, 275 (1920); H. S. Frank and P. T. Thompson, *J. Chem. Phys.*, **31**, 1086 (1959); J. E. Desnoyers and B. E. Conway, *J. Phys. Chem.*, **68**, 2305 (1964).

(7) N. Ise and T. Okubo, *ibid.*, **71**, 1287 (1967).