The calculations are essentially analogous to those made for the room temperature experiment. It is to be noted, however, that K_2, the second dissociation constant of oxalic acid, depends on the temperature in the following way[16]

$$-\log K_2 = (1423.8/T) - 6.5007 + 0.020095T$$

and it is this temperature variation which is responsible for the observed spectrophotometric changes. The heat of formation of the first complex, $NpO_2C_2O_4^-$, was calculated to be 0.0 ± 0.3 kcal.

Direct Evidence for Formation of Anionic Oxalate Complex.—To confirm the spectrophotometric evidence for the existence of anionic oxalate complexes of NpO_2^+, the technique of paper electromigration was employed. The general experimental technique has been described in the literature.[18] In one case an acetate buffer at *p*H 4.5 was used as the supporting electrolyte, in the other case an oxalate buffer, also at *p*H 4.5, was used. Essentially, the technique consists of placing a drop of the test solution, in this experiment, a drop of NpO_2^+ stock solution containing approximately 0.3 mg. of neptunium on the wet filter paper and to observe the migration of the radioactive species in an electric field. A radioautograph made of the paper after allowing migration to proceed for five hours, showed that, in acetate solution, the neptunium moved toward the cathode while in oxalate solution it moved toward the anode proving that in the former medium Np(V) behaves like a cation, while in the latter, Np(V) is bound in an anionic complex.

Other Np(V) Complexes.—Spectrophotometric studies of NpO_2^+ in the presence of other ions are currently under way. Preliminary work shows that spectral changes of the type described here occur in the presence of salicylate and thiocyanate ions. However, the association constants for these ions are smaller by a factor of 10^3 compared with oxalate ion.

Acknowledgments.—It is a pleasure to acknowledge the coöperation of Dr. Harold Strain and Mr. Herbert Diamond in the electromigration experiment and to thank Dr. J. C. Hindman and Mr. J. C. Sullivan of Argonne and Dr. Donald Long of Universal Oil Products for stimulating discussions.

LEMONT, ILL.

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(18) T. R. Sato, H. Diamond, W. P. Norris and H. H. Strain, THIS JOURNAL, **74**, 6154 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

The Interaction of Dienophiles with Aromatic Substances

BY L. J. ANDREWS AND R. M. KEEFER

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It has been demonstrated through spectrophotometric studies that benzene and other aromatic substances interact with maleic anhydride, chloromaleic anhydride and benzoquinone in chloroform solution to form 1:1 complexes which have characteristic absorption spectra in the ultraviolet or visible region of the spectrum. Methods of previous investigations have been used to evaluate equilibrium constants for formation of the complexes. The stabilities of the complexes are enhanced slightly by the presence on the aromatic ring of substituents which increase its electron density. Structures are proposed for the complexes in which the aromatic nucleus functions as an electron donor in coördinating with the dienophile.

Among a large group of polarizable substances which function as electron acceptors in forming addition complexes with aromatic and other unsaturated substances should be included compounds such as maleic anhydride and benzoquinone which serve as dienophiles in the Diels–Alder reaction. As evidence for such interaction may be cited the observation that intense coloration is observed when maleic anhydride[1] or quinones[2] are fused with highly methylated benzenes, diphenylpolyenes and related substances. It should also be recalled that the transient color formation frequently observed to occur during the diene synthesis is ascribed to a diene–dienophile complex which is regarded as an intermediate in the formation of the colorless addition product.[3]

Little attention has been paid to the extent of such interactions in solution, although Michaelis and Granick[4] have demonstrated by spectrophotometric studies that chloranil and benzoquinone interact with phenolic compounds in solution to form 1:1 complexes with characteristic absorption spectra. However no quantitative estimate of the extent of such interactions in solutions has been made, nor has it been demonstrated that dienophiles will undergo coördination with simpler aromatic substances, such as benzene itself, which lack substituents that strongly enhance the electron density of the aromatic nucleus.

Using spectrophotometric procedures similar to those employed previously in studying aromatic addition complexes[5] equilibrium constants for the interaction of benzene with maleic anhydride, chloromaleic anhydride and benzoquinone have now been determined. Additional studies have been made to determine the extent to which the tendency for such interaction is influenced by substituents in the aromatic nucleus. Equilibrium constants for complex formation of anthracene and

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(1) (a) P. Pfeiffer and T. Böttler, *Ber.*, **51**, 1819 (1918); (b) R. Kuhn and T. Wagner-Jauregg, *ibid.*, **63**, 2662 (1930);

(2) (a) P. Pfeiffer, W. Jowleff, P. Fischer, P. Monti and H. Mully, *Ann.*, **412**, 253 (1916); (b) R. Kuhn and T. Wagner-Jauregg, *Helv. Chim. Acta*, **13**, 9 (1930).

(3) For a summary of the pertinent literature see M. C. Kloetzel, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 9.

(4) L. Michaelis and S. Granick, THIS JOURNAL, **66**, 1023 (1944).

(5) (a) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949); (b) L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 5400 (1952) and preceding papers.

of allyl chloride with maleic anhydride have also been determined.

Experimental

Materials.—In general the highest grades of commercially available materials were employed and were purified by recrystallization or fractionation just before use. C.P. Baker chloroform was used without further treatment. As the spectra of solutions of benzoquinone or the anhydrides change slowly with time, only freshly prepared solutions were used in these experiments.

The Absorption Spectrum Measurements.—Chloroform solutions of known concentration of the dienophile and of the aromatic substances were prepared at 25°. Known volumes of these solutions were mixed, and the absorption spectra of the resultant solutions were measured on the Beckman spectrophotometer at 25° against chloroform solutions of the same concentration of aromatic substance as contained in the sample. The dienophile concentration in most of these solutions varied from 10^{-2}–10^{-3} *M*, while the mole fraction of aromatic material in the solvent varied from 0.02–1. In the anthracene-maleic anhydride studies the concentration of anthracene varied from 7×10^{-3}–3.3×10^{-2} *M* and of the dienophile from 1.3×10^{-2}–7×10^{-2} *M*. In the hexamethylbenzene-maleic anhydride studies the hexamethylbenzene concentration varied, from 0.2–0.8 *M* and the maleic anhydride from 4.5×10^{-2}–1.5×10^{-2} *M*.

For most solutions absorption measurements were restricted to the ultraviolet region of the spectrum; although in those cases in which the complex solutions were markedly colored, measurements were extended to the region above 400 mμ.

Results

Figure 1 presents the ultraviolet absorption spectra of maleic anhydride, chloromaleic anhydride and benzoquinone in both benzene and chloroform. In the aromatic hydrocarbon solvent the three dienophiles display major absorption bands in the near ultraviolet region with maxima appearing just below 280 mμ. This high intensity absorption, which is lacking in this region of the spectra of the dienophiles in chloroform solution, is presumed to be indicative of benzene–dienophile complex formation. The results of spectrophotometric studies on a series of solutions of each dienophile in various benzene–chloroform solvent mixtures suggested that equilibria as represented by equation (1)

$$\mathrm{Ar} + \mathrm{D} \rightleftarrows \mathrm{Ar{\cdot}D} \quad K = (\mathrm{Ar{\cdot}D})/(\mathrm{Ar})(\mathrm{D}) \quad (1)$$

were established with respect to the formation of a 1:1 benzene–dienophile complex designated as Ar·D. In these solutions the benzene concentration was much greater than that of the dienophile. Under these circumstances it can be demonstrated[6] that at any given wave length the equilibrium constant for complex formation is related to the benzene concentration by equation (2)

$$1/(\epsilon_A - \epsilon_D) = 1/K(\mathrm{Ar})(\epsilon_C - \epsilon_D) + 1/(\epsilon_C - \epsilon_D) \quad (2)$$

in which ϵ_A is related to the measured optical density, *d*, and to the total molar concentration of both free and complexed dienophile (D_t) by the expression[7] $d = \log_{10} I_0/I = \epsilon_A(D_t)$. The terms ϵ_C and ϵ_D represent, respectively, the extinction coefficient of the complex and of the uncomplexed dienophile.

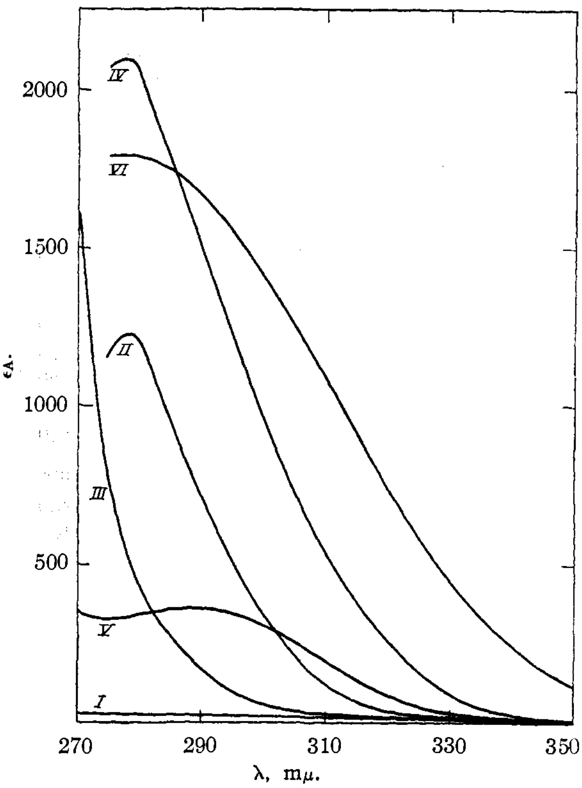

Fig. 1.—Absorption spectrum of maleic anhydride in chloroform (I) and benzene (II); of chloromaleic anhydride in chloroform (III) and benzene (IV); of benzoquinone in chloroform (V) and benzene (VI).

The evaluation of *K* values for the benzene complexes was made by plotting experimentally determined values of $1/(\epsilon_A - \epsilon_D)$ at a given wave length *versus* $1/N_{Ar}$ (N_{Ar} represents the mole fraction of benzene in the chloroform–benzene solvent) for a series of solutions of dienophile in which N_{Ar} varied from 0.02–0.4. The extinction coefficients of the dienophiles in pure chloroform were used for ϵ_D values. As required for 1:1 complex formation the data on graphical analysis according to equation (2) conformed well to straight line plots. Values of *K* and ϵ_C were determined from the slopes and intercepts of these lines over a series of wave lengths in the vicinity of the complex absorption maximum.

In a similar fashion equilibrium constants for the interaction of a number of substituted benzenes, of anthracene and of allyl chloride with these dienophiles were determined. In most of the experiments solutions of relatively high concentration of aromatic substance were used in the spectrophotometric measurements. In these cases the calculated equilibrium constants were based on the expression of concentration of aromatic substance in equation (2) in mole fraction units. The resultant equilibrium constants are designated as K_N in Table I. With anthracene and hexamethylbenzene, because of solubility limitations, only dilute solutions of the aromatic material could be prepared. In these cases the reported values of *K* were based on molar concentrations of aromatic substance and are designated as K_c values in Table I.

The K_C values were evaluated by graphical in-

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[6] J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

[7] One-cm. absorption cells were used for all measurements.

TABLE I[a]

EQUILIBRIUM CONSTANTS FOR COMPLEX FORMATION (25°)

λ, mμ	K_N	ϵ_C	λ, mμ	K_N	ϵ_C
MA–benzene			MA–toluene		
276	0.66	3140	282	0.59	3860
280	.60	3050	286	.58	3720
284	.64	2520	290	.61	3350
290	.67	1780	300	.60	2520
300	.85	730	310	.60	1680
MA–mesitylene			MA–anisole		
290	1.1	3130	300	0.72	2020
298	0.94	3350	310	.80	1830
306	0.94	3350	320	.84	1620
314	1.1	2870	330	.83	1440
320	1.3	2790	340	1.0	960
MA–styrene			MA–dimethylaniline		
306	1.4	1490	400	1.4	1430
310	1.1	1940	414	1.3	1590
315	1.0	1700	420	1.3	1590
320	1.1	1320	440	1.6	1200
330	1.3	840	480	1.9	625
MA–allyl chloride			Quin.–benzene		
252	0.42	1070	315	0.38	2760
254	.35	1060	325	.39	2380
258	.23	950	330	.47	1700
262	.28	540	345	.45	840
CMA–benzene			CMA–anisole		
305	0.62	2120	320	1.2	1680
310	.58	1730	330	1.3	1620
315	.73	1020	340	1.3	1490
320	.57	890	350	1.3	1320
325	.65	510	360	1.4	1100
λ, mμ	K_C	ϵ_C	λ, mμ	K_C	ϵ_C
MA–anthracene			MA–hexamethylbenzene		
400	2.4	173	410	0.13	830
410	1.4	220	415	.14	670
420	1.7	150	420	.18	385
430	1.6	225	425	.22	238

[a] In the table the abbreviations MA, Quin. and CMA refer, respectively, to maleic anhydride, benzoquinone and chloromaleic anhydride.

terpretation of the experimental data at any given wave length according to equation (3)

$$(\mathrm{Ar_t})(\mathrm{D_t})/d[(\mathrm{Ar_t}) + (\mathrm{D_t})] = 1/[(\mathrm{Ar_t}) + (\mathrm{D_t})]K_c\epsilon_C + 1/\epsilon_C \quad (3)$$

a modified form of equation (2) applicable in situation in which the condition (Ar) >> (D_t) does not hold[8] and in which ϵ_D is negligibly small. The terms (Ar_t) and (D_t) represent the total molar concentrations of free and complexed aromatic substance and dienophile, and *d* represents the measured optical density of the corresponding solution.

For most of the aromatic substances studied *K* values for complex formation evaluated at several different wave lengths in the region of the complex absorption maximum were in reasonably good agreement. As a typical example of the method of graphical evaluation of equilibrium constants according to equation (2), plots of some of the data for benzene–chloromaleic anhydride solutions are given in Fig. 2.

In the case of the hexamethylbenzene maleic anhydride complex, the equilibrium constant could not be determined with accuracy from measurements in the neighborhood of the absorption maximum at 350 mμ because of the large magnitude of ϵ_D values (and correspondingly small intercepts in the graphical analysis). The *K* values obtained at higher wave lengths increased somewhat as the wave length shifted further into the visible region. It is possible that these changes in calculated *K* values result from deviations from Beer's law in the absorption of the complex.

In calculating equilibrium constants for the quinone–benzene complex and for the chloromaleic anhydride complexes of benzene and anisole, data taken at the complex absorption maxima (about 280–290 mμ) were avoided because of the relatively high absorption of the uncomplexed dienophiles in these regions. No marked shifts in calculated *K* values with changes in wave length were noted in these cases when data taken at longer wave lengths were used.

An attempt was also made, using the same experimental procedures employed in determining the *K* values of Table I, to evaluate the equilibrium constant for the interaction of hydroquinone and quinone in ethanol solution. The conclusion of Michaelis and Granick[4] that a 1:1 complex was formed was readily confirmed. However, the hydroquinone concentration of the solutions could not be raised sufficiently to reduce the concentration of uncomplexed quinone to the degree required for evaluation of the equilibrium constant.

The Structure of the Complexes.—While the effects of benzene ring substituents on the equilibrium constants for aromatic–dienophile complexes are not marked, the complex stabilities are enhanced by ring substituents which increase the electron density of the aromatic nucleus. Thus the K_N values for complexes of maleic anhydride with mesitylene, anisole and particularly with dimethylaniline are noticeably larger than those for the benzene and toluene complexes. This observation is in accord with the assumption that the aromatic nucleus functions as an electron donor in interacting with the dienophile.

One might conclude that the intense color of the dimethylaniline–maleic anhydride complex results from a specific interaction of the amino group rather than of the aromatic nucleus with the dienophile. However, as Weiss[9] has pointed out, it seems more likely that the amino group and the aromatic nucleus participate as a unit rather than as independent entities in sharing electrons with the maleic anhydride molecule. In favor of this viewpoint may be cited the observation[10] that unlike dimethylaniline, phenylethylamine does not produce a colored solution when it is dissolved in nitrobenzene.

As might be anticipated in view of its susceptibility to other types of addition reactions, anthra-

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(8) *Cf.* R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 1891 (1952).

(9) J. Weiss, *J. Chem. Soc.*, **245** (1942).

(10) R. E. Gibson and O. H. Loeffler, THIS JOURNAL, **62**, 1324 (1940).

cene shows a marked capacity to form a maleic anhydride complex. Styrene forms a more stable complex than does benzene. As in the case of dimethylaniline it seems likely that the electron donor properties of the styrene molecule must derive from the total conjugated system rather than from independent contributions of the aromatic nucleus and the vinyl side chain. It is interesting to note, however, that a compound such as allyl chloride, which contains an isolated double bond, shows a measurable capacity to undergo coördination with maleic anhydride.

As is evidenced by the K values for their interaction with benzene there is no marked difference in the capacity for aromatic complex formation of maleic anhydride, chloromaleic anhydride or benzoquinone. Because of the favorable inductive effect of the halogen substituent chloromaleic anhydride should function more strongly than maleic anhydride as an electron acceptor in this type of interaction. The results of the studies on anisole lend some support to this hypothesis.

In formulating possible structures for these complexes, the observation[11] that benzene and oxalyl chloride interact to form a complex with a characteristic ultraviolet absorption spectrum was recalled. It seemed important to eliminate from consideration the possibility that the maleic anhydride–aromatic complexes were formed by selective coördination of the anhydride function of the dienophile with the aromatic nucleus. This was done on the basis of the observation that benzene solutions of succinic anhydride were found to show no ultraviolet absorption spectrum of the type exhibited by the maleic anhydride complexes.

From a consideration of steric influences as based on an examination of molecular models it seems most reasonable that in these coördination complexes the planes of the rings of the aromatic and dienophile molecules must be parallel. It has previously been demonstrated through kinetic studies that in the Diels–Alder reaction the reacting diene and dienophile molecules must lie in different (and presumably parallel) planes as they approach each other.[12]

A structure for the complexes in which the two carbonyl oxygens of the maleic anhydride or quinone type dienophiles are coördinated at para positions on the aromatic ring is not reasonable because of the large oxygen–oxygen interatomic separation. In a structure for the benzene–maleic anhydride complex, which does not seem in conflict with any available facts, the double bond carbons of the dienophile molecule are centrally located above two carbons para to each other across the aromatic ring. Such a structure could be described as a resonance hybrid based upon contributions from forms of the type

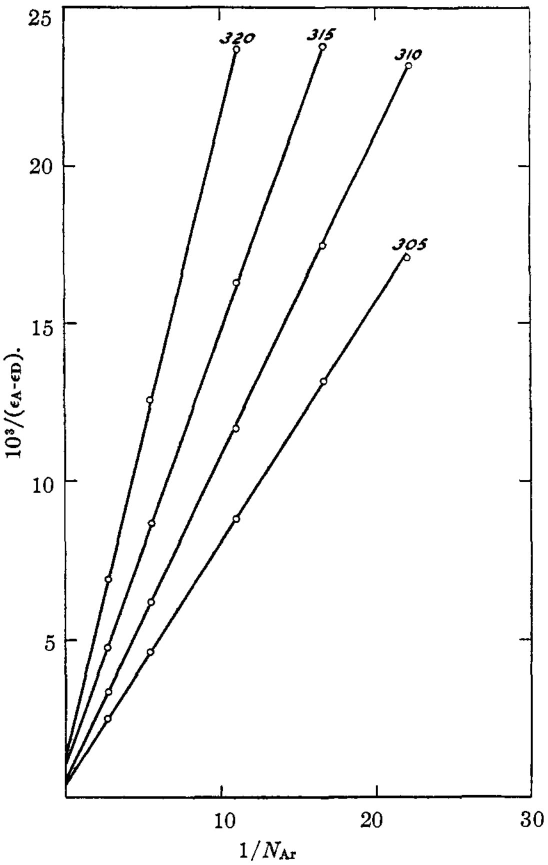

Fig. 2.—Evaluation of K_N for the benzene–chloromaleic anhydride complex at 305, 310, 315 and 320 mμ.

This resonance hybrid structure undoubtedly overemphasizes the degree to which the transfer of electrons from the aromatic nucleus to the dienophile occurs.

NOTE ADDED IN PROOF:—Very recently observations similar to those reported in this paper concerning the spectrum of maleic anhydride in certain aromatic solvents have been reported elsewhere (W. G. Barb, *Trans. Faraday Soc.*, **49**, 143 (1953)).

DAVIS, CALIFORNIA

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[11] B. D. Saskena and R. E. Kagarise, *J. Chem. Phys.*, **19**, 994 (1951).

[12] W. Rubin and A. Wassermann, *J. Chem. Soc.*, 2205 (1950).