

Dissociation of Anthracene Dimer by Solid Acid Catalysts at 25°C

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The uncatalyzed dissociation of anthracene dimer, a reaction in which carbon-carbon bonds are broken, is very slow at room temperature although the equilibrium greatly favors the monomer. However, the dissociation of the dimer in heptane solution and in the absence of oxygen occurs readily in the presence of silica-alumina cracking catalysts. The coked catalyst has greatly reduced activity. Pure alumina has slight activity and silica gel has virtually none. Procedures have been developed for following the rate of dissociation spectroscopically *in situ*. A carbonium ion mechanism is proposed for the catalyzed dissociation.

The dissociation of anthracene dimer is a reaction in which the 9,9' and 10,10' carbon-carbon bonds are broken, resulting in two anthracene molecules. The dissociation is uncomplicated by side reactions. The present work with anthracene dimer was prompted by an article on substituted anthracene dimers (1) in which it was stated that a colorless saturated solution of bis-9-anthraldehyde slowly turned yellow after a trace of *p*-toluenesulfonic acid was added. The authors attributed this to dissociation of the colorless dimer into the colored monomer, but the reaction was not investigated further. Our interest in anthracene dimer was further aroused when we found that the dissociation could be carried out at room temperature over a commercial silica-alumina cracking catalyst. It was considered possible that the acid component of the cracking catalyst could be linked to the rate of dimer dissociation.

Anthracene dimer has a high energy content and is thermodynamically very unstable with respect to the monomer. Although the free energy of formation of the dimer is unknown, heats of formation permit one to estimate a lower limit of the dissociation equilibrium constant.

$$\frac{\Delta H^{\circ}_{298} \text{ (kcal/mole)}}{(2)}$$

Anthracene dimer (s)	73.2
Anthracene (s)	28.8

Hence, for the reaction, Anthracene dimer = 2 Anthracene, $\Delta H^{\circ}_{298} = -15.6$ kcal. The equilibrium constant may be derived from the equation

$$\log_{10} K_T = \frac{-(\Delta H^{\circ}_T - T\Delta S^{\circ}_T)}{2.3RT}$$

At 298°K,

$$\begin{aligned} \log_{10} K_{298} &= \frac{15.6 \times 10^3 + (298)(\Delta S^{\circ}_{298})}{(2.3)(1.98)(298)} \\ &= 11.5 + \frac{\Delta S^{\circ}_{298}}{4.6} \end{aligned}$$

The entropy change for this reaction is undoubtedly positive, and therefore the dimer dissociation equilibrium is greatly in favor of the monomer. Nevertheless the rate of thermal dissociation at moderate temperatures is slow. Rates of dissociation in anisole and phenetole solution have been measured in the range 154° to 170°C (3), and extrapolation of these data gives a half time of many years for dissociation at room temperature. This extremely slow thermal dissociation is a favorable circumstance for measurement of catalytic dissociation of the dimer at room temperature.

Ultraviolet spectroscopy was employed to follow the dissociation of the dimer. This made it necessary to select a paraffin solvent; normal heptane proved suitable. In this solvent the solubility of the dimer is only a few milligrams per liter and there-

fore the experiments were performed using a slurry of the dimer and catalyst.

EXPERIMENTAL

Anthracene Dimer

Two liters of isooctane were placed in a 3-liter three-necked round-bottomed flask fitted with a reflux condenser, a quartz finger containing a General Electric AH-4 mercury arc lamp, and a stirrer. Nitrogen was passed through a tee at the top of the condenser. The isooctane was refluxed with stirring for 10 min while passing nitrogen through the tee. The heating element was then turned off, the flask was opened momentarily to add 2 g of Eastman Kodak Co. 480-X "blue-violet fluorescent" anthracene, and the mercury lamp was turned on. After a few minutes a white precipitate began to form, anthracene dimer being rather insoluble in isooctane. Irradiation was continued for 6 hr, the dimer was filtered off and dissolved in hot benzene, the solution was filtered while hot, cooled in ice, and the crop of crystals was filtered. The product was dried in a vacuum desiccator, and was stored over Drierite. The dimer obtained in this way was perfectly white. The ultraviolet spectrum of a saturated solution in isooctane showed no indication of the presence of benzene, anthracene, or other impurity.

The dimer synthesis must be carried out in the absence of air to avoid photooxidation of anthracene. For this reason, the solvent was boiled to expel dissolved air, and the solution was blanketed with nitrogen during irradiation. If these precautions were not observed, the dimer precipitate was pale yellow, and this color was not completely removed by recrystallization from benzene. Apparently on irradiation of anthracene in the presence of oxygen the colorless photooxide is formed first (4). The photooxide then decomposes into various colored oxidation products (5). The dimer does not have a definite melting point, because it undergoes more or less dissociation on heating. The observed melting point depends on the rate of heating (6).

Ultraviolet Absorption Spectrum of Anthracene Dimer

V. S. Medvedev *et al.* (7) investigated the ultraviolet absorption spectrum of dimers of 9, 10-substituted anthracenes and concluded that carbon-carbon bonding occurs at the 9,9' and 10,10' positions. C. A. Coulson *et al.* (8) obtained spectra of the dimer in alcoholic solution, and found a strong band at 2175 Å and a group of bands between 2600 and 2850 Å. These authors made a quantitative comparison of the dimer spectrum with that of *o*-xylene and arrived at the same structure as that proposed by Medvedev *et al.*

In the present study, the spectrum of a sample of the dimer (which had been thoroughly outgassed at room temperature) in *n*-heptane solution showed a strong band at 2175 Å. Three additional characteristic bands are observed in a saturated solution at 2640, 2720, and 2830 Å in acetonitrile (which is a better solvent for the dimer), in agreement with the spectra of Coulson *et al.*

Solubility of Anthracene Dimer in n-Heptane

The solubility of the dimer in *n*-heptane was calculated based on Coulson's value of the extinction coefficient of the dimer at 2175 Å, $\log \epsilon = 4.3$ (where ϵ has the units liters/mole cm), and on the absorption spectrum of the saturated solution in *n*-heptane (see Fig. 1). From these data a solubility of 0.00855 g/liter was obtained.

Ultraviolet Spectrophotometric Analysis for Anthracene

Analysis for anthracene formed in dissociation of anthracene dimer was performed by ultraviolet spectrophotometry in a Cary Model 11 or Model 14 Recording Spectrophotometer. It is conveniently done either (1) with the absorption peak at 2525 Å with an extinction coefficient of 1250 liters/g cm or (2) with the peak at 3750 Å, with an extinction coefficient of 45.5 liters/g cm. The intense peak at 2525 Å permits detection of anthracene in very dilute solution. For example, an optical den-

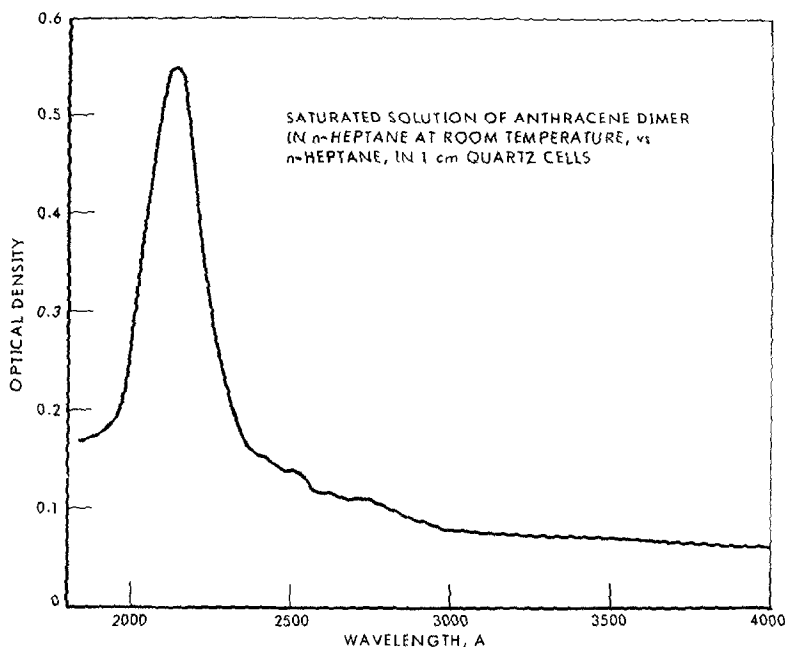


Fig. 1. Spectrum of anthracene dimer.

sity of 0.03 above the blank in a 1-cm cell at that wavelength corresponds to an anthracene concentration of 2.4×10^{-5} g/liter.

Reagents and Materials

n-Heptane. Phillips Petroleum Co. pure n-heptane was purified in the following way. A gaseous mixture of nitrogen dioxide and its dimer was bubbled into the hydrocarbon from the cylinder until the hydrocarbon took on an orange color which did not fade on standing for a few minutes. Ascarite was then added to absorb most of the excess nitrogen oxides, and the hydrocarbon was passed through Davison commercial silica gel in a column 30 cm in length by 6 cm in diameter, with a layer of Ascarite at the top. Chromatographed hydrocarbon was stored over calcined silica gel in a 1-gallon bottle having a ground glass dispensing stopper protected with a Drierite tube. The ultraviolet spectrum of a batch of purified hydrocarbon was always obtained before use, to make sure of a sufficiently low optical density. An optical density compared to water, in 1-cm quartz cells, of 0.3 or less at 2000 Å and a few

hundredths at wavelengths above 2500 Å was regarded as satisfactory.

Helium or nitrogen dry and oxygen-free. Water-pumped nitrogen or cylinder helium was passed over freshly hydrogen-reduced copper oxide turnings at 600°C, then through a liquid nitrogen trap containing a sintered glass disc, to remove water vapor.

Gum rubber tubing. Pure gum rubber tubing $\frac{3}{16}$ -inch ID, $\frac{1}{8}$ -inch wall, containing no carbon black or other filler or pigment, from Standard Rubber Co. was employed in some experiments, to conduct inert gas, or, in lengths of 2 or 3 cm to make connections in the glass apparatus.

Pure silica gel. Prepared from purified sodium silicate at pH 5.

Low alumina silica-alumina. Contained 0.15% Al, and less than 0.003% Na.

MSA-1 silica-alumina. From American Cyanamid Co., containing 12.7% Al_2O_3 . It was elutriated to remove fines smaller than 325 mesh.

MSA-3 silica-alumina. Aerocat, American Cyanamid Co. Organic contaminants were removed by calcining in air at 550°C for 5 hr. Analysis = 22.1% Al_2O_3 , 0.92% SiO_2 , 0.032% Fe, and 0.009% Na.

Pure alumina. Prepared by hydrolysis of aluminum isopropylate. Contained 0.20% Cl, < 0.002% Si.

***n*-Butylamine.** From Eastman Kodak Co., purified by distillation.

Procedure for Dimer Dissociation Tests

The three outgassed components, dimer, catalyst, and solvent were brought together in a Pyrex tube under vacuum and the tube was sealed off in vacuum. After the desired time of reaction a 1-ml sample of the supernatant solution was removed and mixed with 20 ml of *n*-heptane. Then 0.2 ml of *n*-butylamine was added to the tube and mixed for a minute or two to displace anthracene from the catalyst, and a second 1-ml sample of the supernatant solution was removed and mixed with 20 ml of *n*-heptane solvent. The two solutions thus prepared were then analyzed in the multiple cell attachment of the spectrophotometer.

In an alternative technique spectrophotometric analyses were made periodically on the solution *in situ*. Details of the experimental procedures are given below:

Experiment 1. No catalyst was used in this experiment. Dimer was weighed into tube A in Fig. 2A, and was evacuated at

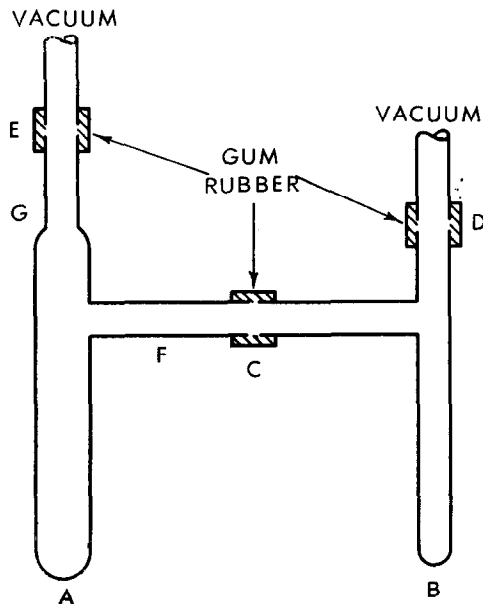


FIG. 2A. Assembly for Expt. 1, thermal dissociation of anthracene dimer.

room temperature. With a pinch clamp at C closed, *n*-heptane was outgassed in B; then, with D and E pinched off and C open, the *n*-heptane was distilled into A and the tube was sealed off at F and G.

Experiments 2-7. The assembly for these tests is shown in Fig. 2B. Catalyst was added to the tube at A, was outgassed at

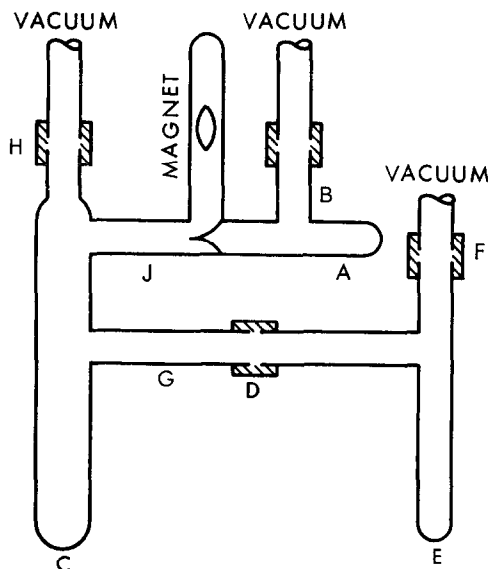


FIG. 2B. Assembly for Expts. 2-7.

550°C for 15 min, and sealed off at B. Dimer was put into the tube at C taking care to avoid getting it on the wall of the tube where the seal was to be made later. The assembly was then attached to the vacuum line, and with the pinch clamp at D closed, the dimer was evacuated at room temperature. *n*-Heptane was outgassed in E, then was distilled into C with pinch clamps F and H closed, and the tube was sealed off at G. With C in liquid nitrogen and H open to the pump, the tube was sealed off below H. Catalyst was transferred into C through the break seal, and the catalyst side tube was sealed off at J with C in liquid nitrogen.

Experiment 8. An all-glass reaction vessel similar in design to that in Fig. 2B was used.

Experiment 9. In Experiments 9 and 10, the reaction was followed by spectroscopy

in situ in an all-glass reaction vessel. Figure 2C shows the assembly employed for Experiment 9, which has a quartz absorption cell on a sidearm. The MSA-3 silica-alumina catalyst (0.1818 g) was heated to 550°C in air and evacuated at 550°C for 4 hr; 9.0 mg of dimer and 10 ml of *n*-heptane were used.

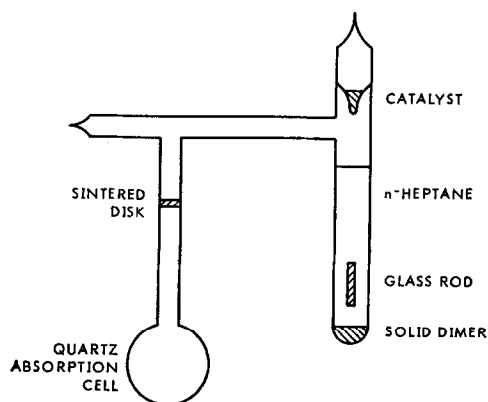


FIG. 2C. Dimer dissociation by spectroscopy *in situ*. Reaction tube in Expt. 9 before start of reaction.

Experiment 10. The assembly, shown in Fig. 2D, differed from that in Experiment 9 in having a larger reaction vessel (A) to accommodate a larger volume of *n*-heptane (25 ml), and in having a glass-enclosed

iron slug for the double purpose of opening the break seal and stirring the reaction mixture with a magnetic stirrer. The calcined MSA-3 silica-alumina catalyst (0.0800 g) was heated to 550°C in air, and evacuated at that temperature for 15 hr. The dimer (12.9 mg) was evacuated at room temperature as usual.

EFFECT OF VARIOUS CATALYSTS

Results of these tests are given in Table 1. Experiment No. 1 shows that thermal dissociation is indeed extremely slow. The pure silica gel also had low activity (Experiment 2), the amount of dissociation being only double that for the "thermal" experiment. This result is as expected since pure silica gel is an extremely feeble acid. Its catalytic activity for cracking of various hydrocarbons in the range 450° to 550°C (9) and for isomerization of cyclopropane at 147°C (10) is very low.

Copolymerization of as little as 0.1% alumina with silica has long been known to bring about a very marked increase in catalytic cracking activity (11). In Experiment No. 3 with silica-alumina containing 0.15% Al the catalyst proved to be about twice as active as pure silica gel. The catalyst remained white throughout the reaction.

MSA-1, one of the commercial silica-

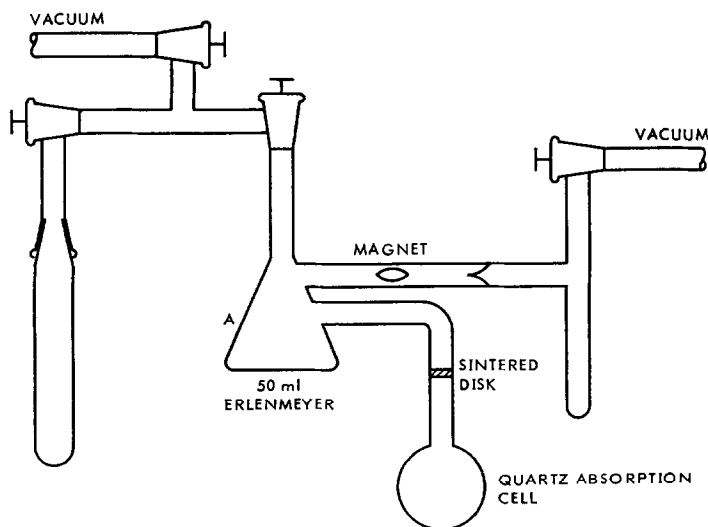


FIG. 2D. Dimer Dissociation with spectroscopy *in situ*. Apparatus for Expt. 10.

TABLE I
 ANTHRACENE DIMER, SINGLE-POINT EXPERIMENTS^a

Experiment number	Catalyst		Dimer charged (mg)	Time of reaction (min)	Dimer dissociated		Anthracene at end of run		Color of catalyst-anthracene
	Type	Surface area (m ² /g)			Weight (g)	(mg)	(mg per g cat.)	mg/liter of solution	
1	None	—	7.6	1440	0.0042	—	—	—	—
2	SiO ₂ gel	739	0.2232	1455	0.0085	0.038	0.572	0.026	White
3	0.15% Al ₂ O ₃ /SiO ₂	525	0.2567	1800	0.027	0.105	3.20	0.43	White
4	12.7% Al ₂ O ₃ /SiO ₂	619	0.1974	240	2.16	11.0	240	4.90	Green
5	22% Al ₂ O ₃ /SiO ₂	526	0.2041	240	2.46	12.1	280	5.20	Green
6	Alumina	222	0.2080	240	0.0804	0.38	2.61	0.32	Tan
7	Coked	—	—	—	—	—	—	—	—
	22% Al ₂ O ₃ /SiO ₂	—	0.1984	240	0.0935	0.47	7.48	0.28	Gray
8	γ-irrad. SiO ₂ gel	—	0.3845	1500	0.0154	0.040	2.10	0.013	White

^a Room temperature, 5 ml *n*-heptane.

alumina catalysts, containing 12.7% alumina, was 100 times more active for dimer dissociation than was the low alumina silica-alumina.

MSA-3, the commercial high alumina catalyst containing 22% alumina had the highest activity of all.

The sample of pure alumina from aluminum isopropylate was tested for dimer dissociation activity. This alumina had a specific surface of 222 m²/g and was found to have a titer of 95 μmoles/g based upon the absorption of trimethylamine vapor (12). It possessed considerably more surface acidity per square meter than MSA-1 silica-alumina, which had a titer of 135 μmoles/g and a specific surface of 646 m²/g. The failure of alumina to show a high catalytic activity suggests that it may be deficient in certain special, perhaps highly acid, sites, although its total acidity is high. The appearance of the alumina during the course of dimer dissociation bears out this suggestion. Whereas the dissociation on silica-alumina catalyst is accompanied by the appearance of "anthracene green" on the catalyst, in the case of alumina a tan color appeared during the reaction. Adsorbed anthracene may have different colors on qualitatively different adsorption sites.

To prepare the coked catalyst used in Experiment 7, isooctane was cracked over MSA-3 silica-alumina until the catalyst became light brown in color. It was then heated to 550°C briefly in a stream of nitrogen. The catalyst was then dark gray, and contained only 0.3% C. A portion was evacuated for 2 hr at 550°C, and was found to have 4% of the dimer dissociation activity of fresh MSA-3. This experiment shows that coke is a very powerful inhibitor of dimer dissociation, and suggests that coke formation and dimer dissociation occur preferentially on the most acidic sites.

Catalytic activity resulting from defects created in a solid structure by high energy radiation is of interest. The results reported on the effect of neutron irradiation of silica gel on double-bond isomerization of 1-hexene, and on cumene cracking are somewhat ambiguous (13), and it was felt that dimer

dissociation at room temperature is better suited to the study of catalytic properties of solid structures which may well be thermally labile. One experiment was made in this direction in which the practically inactive silica gel was irradiated with 1.35×10^7 roentgens of gamma radiation from Co⁶⁰ at Stanford Research Institute. Before exposure the gel (0.385 g) was evacuated at 550°C for 5 hr in a Pyrex tube fitted with a break-seal, and then the tube was sealed off under vacuum.

The irradiated gel was mixed with outgassed dimer and *n*-heptane for 25 hr at room temperature, and was found to have the same dimer dissociation activity as the original gel (compare Experiment 8 with Experiment 2, Table 1).

DIMER DISSOCIATION RATE MEASUREMENTS BY SPECTROSCOPY *in situ*

A successful *in situ* procedure would provide for removing samples for analysis without admitting air. It would also allow kinetic data to be collected with little effort compared with that of many single point experiments.

The anthracene absorption spectrum is fortunately well suited to measurement of changing anthracene concentration in an absorption cell of fixed size attached to the reaction vessel. The 2525-Å band with an extinction coefficient of 1250 liters/g cm may be used in the early part of the dimer dissociation, when the anthracene concentration is low. Later, as the concentration of anthracene in solution increases, the longer wavelength bands may be used, with extinction coefficients in the range 6 to 45 liters/g cm.

Two experiments were made with spectroscopy *in situ*. The apparatus and technique for loading the reaction tubes in these experiments are given in detail. Gum rubber was not employed in the loading manipulations.

The first *in situ* experiment, Table 2, Experiment 9, was made with a quartz adsorption cell sealed to a sidearm on the reaction tube to permit observation of the 2525-Å anthracene band, and a coarse sintered glass disk sealed into the sidearm to

TABLE 2
DIMER DISSOCIATION RATES BY SPECTROSCOPY
in situ

<i>Experiment 9</i> 0.1818 g MSA-3 silica-alumina 9.0 mg anthracene dimer 10 ml <i>n</i> -heptane		
Time (min)	Anthracene in supernatant solution (mg/liter)	Anthracene in supernatant solution (mg/g catalyst)
2	1.88	0.104
10	20.9	1.15
20	52	2.86
35	96	5.28
50	126	6.94
60	147	8.09
75	175	9.62
91	193	10.6
105	201	11.1
120	207	11.4

At 121 min, the tube was opened, *n*-butylamine was added, and the total anthracene formed was found to be 13.7 mg/g catalyst.

<i>Experiment 10</i> 0.080 g MSA-3 silica-alumina 12.9 mg anthracene dimer 25 ml <i>n</i> -heptane		
Time (min)	Anthracene in supernatant solution (mg/liter)	Anthracene in supernatant solution (mg/g catalyst)
3.25	Faint trace	
15	1.20	0.38
30	5.18	1.62
45	10.1	3.16
62	16.1	5.04
76	25.1	7.83
105	34.5	10.8
135	46.9	14.6
191	64.1	20.0
252	84.0	26.3
312	122	38.2
372	149	46.5
432	174	54.7

At 2882 min, the tube was opened, *n*-butylamine was added, and total anthracene formed was found to be 108.7 mg/g catalyst.

prevent catalyst and solid dimer from getting into the cell.

Measurements of the anthracene content of the solution during the reaction are given in Table 2 and Fig. 3. The curve in Fig. 3 indicates a gradual slowing of the reaction rate with time.

In the final experiment, Table 2, Experiment 10, further improvements were made. A larger quantity of solvent was employed in order to decrease the relative amount of anthracene adsorbed on the catalyst and

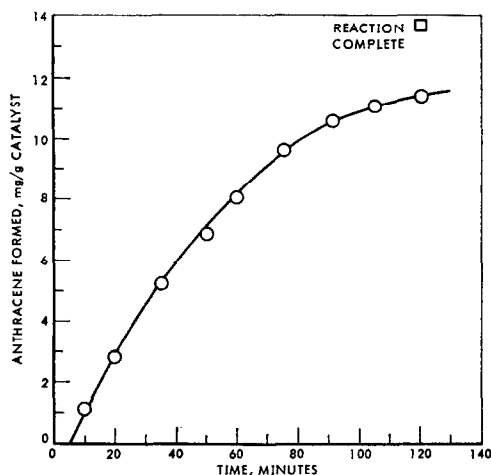


FIG. 3. Dimer dissociation by spectroscopy *in situ*, Expt. 9.

thus maintain a more nearly constant amount of active surface for dimer dissociation. The reaction mixture was stirred magnetically to avoid shaking by hand. A less porous sintered glass disk was used to reduce the clouding of the cell windows by dimer and catalyst.

The data obtained in Experiment 10 are given in Table 2 and Fig. 4. A faint trace of anthracene was found in the spectrum at

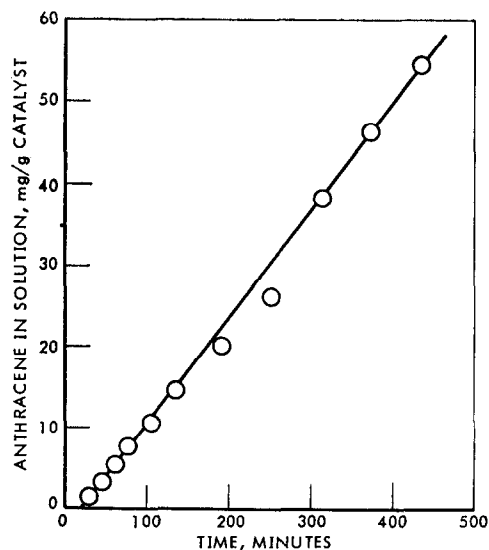


FIG. 4. Dimer dissociation by spectroscopy *in situ*, Expt. 10.

3.25 min, and easily measurable quantities at the next time of observation, 15 min, and thereafter. After 15 min the 2525 Å band became too strong to be usable, and the measurements through 432 min were made on one or another of the bands in the 3000–3800 Å system.

It is noteworthy that the dissociation rate remained constant for an extraordinarily long period, up to 432 min, as is seen in Fig. 4. The implication is that the amount of active catalyst surface remained constant during that time. The zero order rate may be accounted for by the fact that the constant dimer concentration in solution maintains a constant quantity of dimer adsorbed on the catalyst at all times.

The catalyst eventually assumed a yellowish green tinge unlike the pure "anthracene green" (14). A very slow air leak into the absorption cell may have developed. The final point (Table 2) obtained after opening the cell at 2882 min and adding *n*-butylamine shows that the reaction slowed down markedly after the 400-min period of constant rate.

MECHANISM OF ACID-CATALYZED DIMER ASSOCIATION

The reaction may be considered as resulting from electron shifts induced by the approach of a proton to the dimer molecule. The net result of these shifts is likely the liberation of an anthracene molecule with the green anthracene carbonium ion (14) left behind on the catalyst. The carbonium ion may then lose a proton and desorb as anthracene. This mechanism is supported by the studies of Brouwer (15). He found that another aromatic compound, perylene, when adsorbed on a silica-alumina catalyst, gives an ESR spectrum corresponding to that observed for this ion in sulfuric acid solution. It was thus confirmed that aromatic hydrocarbons may

indeed form positive ions upon adsorption on silica-alumina.

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