TABLE IV

EFFECT OF α-PHENYL SUBSTITUTION ON SAPONIFICATION AND ACID HYDROLYSIS

	Saponification		Acid hydrolysis	
	$\Delta \log k$	ΔE	$\Delta \log k$	ΔE
Acetate → phenylacetate	+ .1642	− 600	− .4907	− 100
Propionate → hydratropate	− .6460	+ 700	−1.1338	+ 600
Butyrate → phenylethylacetate	− .8409	+1000	−1.2281	+ 700
Phenylacetate → diphenylacetate	−1.2561	+1900	−1.4657	+1600

base-catalyzed reaction, but only half as fast when the acid catalyst is employed. It is also substantiated by noting that in both processes the introduction of a phenyl group into the alpha position causes a much greater effect when another substituent is already present on the same carbon atom. This is shown in Table IV.

Unfortunately, the data for esterification are not sufficiently complete to allow many deductions, but apparently this process is similar to that of acid hydrolysis in that the steric effect due to phenyl substitution always outweighs the inductive influence, even when such substitution takes place on the terminal carbon atom. The fact that phenylacetic, hydrocinnamic and γ-phenylbutyric acids esterify with almost identical rates is perhaps better explained as a fortuitous balance between inductive and steric effects than as caused by ring formation.[6]

Summary

The kinetics of acid catalyzed hydrolysis in 70% acetone has been studied for ethyl phenylacetate, ethyl hydrocinnamate, ethyl γ-phenylbutyrate, ethyl δ-phenylvalerate, ethyl hydratropate, ethyl phenylethylacetate, ethyl diphenylacetate and ethyl cyclohexylacetate.

The introduction of a phenyl group into an aliphatic ester results in a decrease in the reaction rate for all esters studied, even though the phenyl group acts as an electron sink, and should cause an increase in the rate of hydrolysis. The results may be explained on the assumption that the steric effect of the phenyl group always outweighs its inductive effect for this process.

A comparison is made of the effect of phenyl substitution on the processes of acid hydrolysis, saponification and esterification.

KNOXVILLE, TENN. RECEIVED JUNE 8, 1942

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Reduction of Unsaturated Hydrocarbons at the Dropping Mercury Electrode. II. Aromatic Polynuclear Hydrocarbons[1]

BY S. WAWZONEK AND H. A. LAITINEN

Aromatic compounds possessing a high degree of resonance, such as benzene, do not undergo reduction at the dropping mercury electrode. On the other hand, aromatic polynuclear hydrocarbons showing a diminished degree of resonance are reducible. The polarographic reduction of such hydrocarbons is described in the present paper.

Results

The behavior of various aromatic polynuclear hydrocarbons was studied in a 0.175 *M* tetrabutylammonium iodide, 75% dioxane solution.[1] A summary of the observed half-wave potentials and individual diffusion current constants is given in Table I.

In general, all of the hydrocarbons gave well-defined reduction waves similar to that shown in Fig. 1 for 3-methylcholanthrene. Exceptions to this behavior were treated in the following manner. For compounds (phenanthrene and pyrene) showing two waves of equal height close together such as those shown in Fig. 2 for phenanthrene, the half-wave potentials were calculated by using one-fourth and three-fourths of the total diffusion current. In the table for such cases only the total diffusion current is reported even though two waves were obtained. For compounds (chrysene and 3,4-benzpyrene) which gave indefinite waves such as that shown in Fig. 3 for 3,4-benzpyrene, only the total diffusion current is given. For indene which gave a wave at a potential too negative to be measured, the starting point of the wave is given.

---

(1) Paper I, Laitinen and Wawzonek, THIS JOURNAL, **64**, 1765 (1942). This paper was presented before the Division of Organic Chemistry of the American Chemical Society at the Buffalo meeting, September, 1942.

TABLE I

HALF-WAVE POTENTIALS AND DIFFUSION CURRENT CONSTANTS OF VARIOUS COMPOUNDS IN 0.175 *M* TETRABUTYLAMMONIUM IODIDE–75% DIOXANE

Compound	$\pi_{1/2}$ volts vs. S. C. E.			i_d microamperes		*C, millimoles/* liter	i_d/*C, microamperes/ millimole*/liter	
Naphthalene		2.49		5.19		1.01	5.14	
		2.51		10.40		2.02	5.15	
1,2-Dihydronaphthalene		2.57		9.55		2.154	4.44	
Acenaphthene		2.57		5.46		1.11	4.92	
		2.58		10.85		2.22	4.89	
Indene		starting point 2.54						
3-Phenylindene		2.33		4.28		9.12	4.69	
		2.32		8.40		1.823	4.61	
Fluorene		2.65		7.50		1.33	5.65	
Biphenyl		2.70		5.19		0.745	6.96	
Phenanthrene		2.46	2.71	19.9		2.252	8.84	
		2.44	2.67	14.1		1.376	10.25	
9,10-Dihydrophenanthrene		2.62		6.70		0.932	7.18	
Chrysene		....		14.3		1.11	12.88	
Pyrene	2.10	2.46	2.67	2.38	3.89	0.740	3.22	5.25
	2.10	2.47	2.69	4.77	8.26	1.580	3.22	5.59
Anthracene		1.94		4.17	(3.48)	0.933	4.47	
1,2-Benzanthracene		2.03	2.54	6.80 7.53	(5.73)	1.66	4.10	4.54
1,2,5,6-Dibenzanthracene		2.07	2.53	3.18 5.83	(2.18)	0.773	4.12	7.55
9,10-Dimethyl-1,2-benzanthracene		2.05	2.53	3.62 3.78	(2.85)	.875	4.14	4.32
3-Methylcholanthrene		2.11	2.51	4.86	5.44	1.313	3.70	4.15
3,4-Benzpyrene		1.88	....	2.71	4.52	0.966	2.72	4.54

The reduction of anthracene gave a wave of constant diffusion current of 3.48 microamperes which, at more negative potentials, increased to 4.17 microamperes. The larger value is probably the true diffusion current since it is closer to that observed for phenanthrene (5.15 microamperes). A similar phenomenon occurred with the substituted anthracenes. A small wave always preceded the second reduction wave as shown in Fig. 4 for 9,10-dimethyl-1,2-benzanthracene. The figures in parentheses in the table are the lower diffusion current values used in calculating the half-wave potential of the first wave. The figures without parentheses include the small wave.

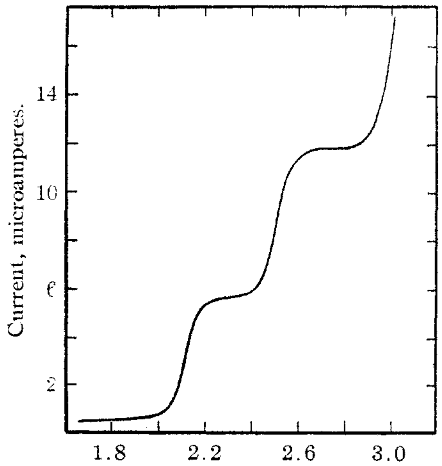


Fig. 1.—Curve for 0.001313 *M* 3-methylcholanthrene in 0.175 *M* $(C_4H_9)_4NI$, 75% dioxane.

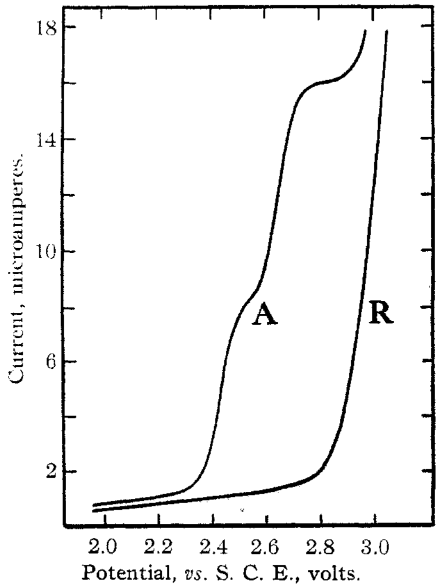


Fig. 2.—Curves in 0.175 *M* $(C_4H_9)_4NI$, 75% dioxane; R, residual current; A, 0.001376 *M* phenanthrene.

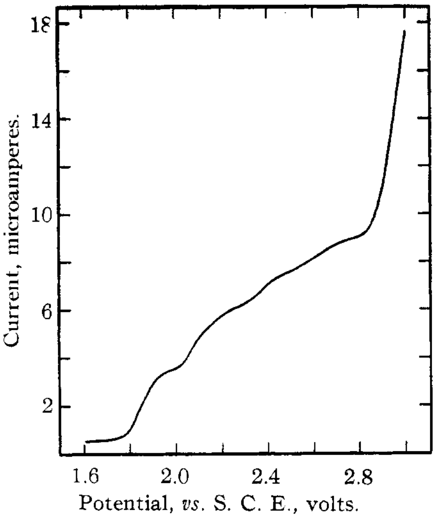


Fig. 3.—Curve for 0.000966 *M* 3,4-benzpyrene in 0.175 *M* $(C_4H_9)_4NI$, 75% dioxane.

The half-wave potential was found to be independent of the concentration of the hydrocarbons. From this behavior it is assumed that the half-wave potential is independent of the *p*H of the solution, as was the case with the phenyl substituted olefins and acetylenes.[1]

The diffusion current was proportional to the concentration in every case studied. An apparent exception is phenanthrene but in this case two different samples of phenanthrene were used. One sample (diffusion current constant of 10.25) was obtained from Gesellschaft für Teervertung while the other (diffusion current constant of 8.84) was prepared by purifying crude phenanthrene by the method of Bachman.[2] It is evident that the polarographic method offers a possible quantitative procedure for the determination of these hydrocarbons in the absence of more readily reducible substances.

Comparison of the diffusion current constants and of the half-wave potentials for the various hydrocarbons indicates that the reduction resembles the phenomenon of the addition of alkali metals to aromatic polynuclear hydrocarbons or their reduction by alkali metals and alcohol. Polarographic data likewise offer a means of determining the arrangement of the double bonds in the various nuclei.

The reduction of naphthalene involved only two electrons and must take place by a 1,4-mechanism since 1,2-dihydronaphthalene was reducible at a more negative potential. The low diffusion current obtained in the latter case was probably due to the presence of some 1,4-dihydronaphthalene which is not reducible at the dropping mercury electrode. The electroreduction of a double bond conjugated with a phenyl group is apparently not affected by its presence in a ring since the value of 2.57 volts obtained for 1,2-dihydronaphthalene is very close to the value obtained for β-methylstyrene (2.54 volts).[1] Tetralin, the reduction product from 1,2-dihydronaphthalene, was not reducible at the electrode. Acenaphthene was reduced similarly to naphthalene since it gave a wave involving two electrons.

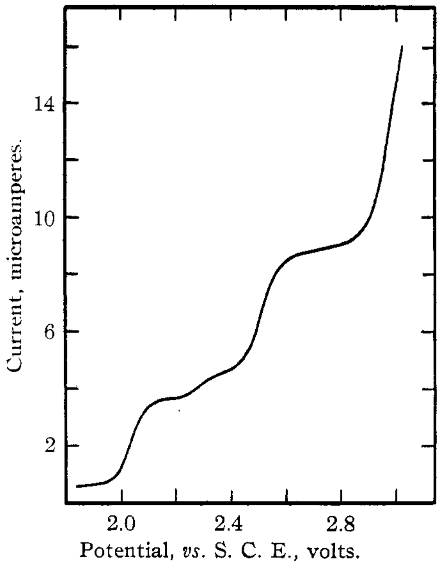


Fig. 4.—Curve for 0.000875 *M* 9,10-dimethyl-1,2-benzanthracene in 0.175 *M* $(C_4H_9)_4NI$, 75% dioxane.

Indene gave a wave at a potential too negative to be evaluated. This behavior is probably due to resonance of the double bond in the five-membered ring. The resonance apparently disappears or is diminished with the introduction of a phenyl group into the ring as it is shown by the more positive value of 2.32 volts obtained for 3-phenylindene. This value would point to the conjugation of the double bond with the phenyl group since the value is approximately equal to the value of 2.27 volts obtained for 1,1-diphenylethylene. Reduction of a double bond in the other position would certainly give a value closer to that of 1,2-dihydronaphthalene or β-methylstyrene. Hydrindene did not reduce at the dropping mercury electrode.

The reduction of biphenyl and fluorene seems to be similar in nature. The course of the reduction is probably through a 1,4-addition like that proposed for the reaction of lithium with biphenyl.[3]

---

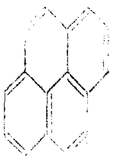
(2) W. E. Bachman, THIS JOURNAL, **57**, 557 (1935).

(3) Schlenk and Bergmann, *Ann.*, **463**, 1–97 (1928).

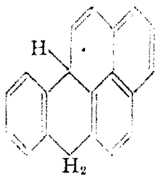
Phenanthrene gave two waves involving two electrons each, with the first wave at 2.44 volts corresponding to the reduction of the 9,10-double bond since 9,10-dihydrophenanthrene reduces at 2.62 volts, a value approximately equal to the 2.67 volts observed for the second wave of phenanthrene. This second reduction wave corresponds to that observed for biphenyl and fluorene, and probably involves a 1,4-reduction in one of the rings similar to the 1,4-addition of lithium to biphenyl observed by Schlenk and Bergmann.[3]

Chrysene gave rather ill-defined waves starting at 2.18 volts with a diffusion current constant of 12.88 microamperes per millimoles per liter. This indicates the introduction of six electrons, two for either the 5,6- or the 11,12-double bond, two for the resulting substituted naphthalene nucleus and two for the resulting substituted dihydrophenanthrene.

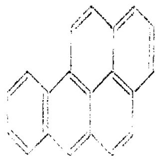
Pyrene gave three waves involving two electrons each. The first wave, at 2.10 volts, corresponds to that observed for stilbene[1] at 2.14 volts and must be due to the reduction of the 1,2-double bond. The remaining two waves at 2.46 and 2.69 volts are identical with the two waves observed for phenanthrene at 2.46 and 2.71 volts, respectively. A structure for pyrene which would fit these facts is shown by formula A and is in agreement with ozonolysis studies carried out with this compound.[4]



A



B



C

Anthracene gave a wave at 1.94 volts involving two electrons and a 1,4-reduction at the 9,10-positions. Substituted anthracenes, such as 1,2-benzanthracene, 1,2,5,6-dibenzanthracene, 9,10-dimethyl-1,2-benzanthracene and 3-methylcholanthrene, which possess carcinogenic properties, were also studied. All showed one half-wave potential value approximately equal to that for anthracene and another of 2.53 volts, which corresponds to the reduction of the resulting naphthalene residue. This latter value is apparently a very characteristic reduction potential for the naphthalene nucleus. For 3,4-benzpyrene the first wave at 1.88 volts, involving two electrons, indicates a reduction similar to that occurring in anthracene. This type of reduction is likewise indicated by a second wave of two electrons, which would necessarily be the reduction of the naphthalene residue in structure B. The total reduction is in agreement with structure C proposed for 3,4-benzpyrene by Cook and Hewett[5] on the basis of absorption spectra.

Experimental

The conditions and electrode used were exactly the same as described in the first paper of this series.[1]

Materials.—Naphthalene, tetralin, acenaphthene, indene, 3-phenylindene, fluorene, biphenyl, phenanthrene, chrysene and pyrene were obtained from stock and purified before using. Anthracene and all carcinogenic hydrocarbons were obtained from Eastman Kodak Company and used without further purification. 1,2-Dihydronaphthalene,[6] 9,10-dihydrophenanthrene[7] and hydrindene[8] were prepared by appropriate methods given in the literature.

Summary

A polarographic study has been made of the reduction of certain aromatic polynuclear hydrocarbons.

The compounds gave half-wave potentials which were independent of their concentration and characteristic of certain structures. The diffusion current was found to be proportional to the hydrocarbon concentration. The polarographic method has been shown to be useful in the quantitative determination of the hydrocarbons and in determining the arrangement of double bonds in their various rings.

URBANA, ILLINOIS

RECEIVED JULY 9, 1942

---

(4) Vollmann, Becker, Corell and Streeck, *Ann.*, **531**, 1-160 (1937).

(5) Cook and Hewett, *J. Chem. Soc.*, 400 (1933).

(6) Tiffeneau and Orechow, *Bull. soc. chim.*, [4] **27**, 787 (1920).

(7) Durland and Adkins, THIS JOURNAL, **59**, 135 (1937).

(8) V. Braun, Arkuszewski and Kohler, *Ber.*, **51**, 291 (1918).