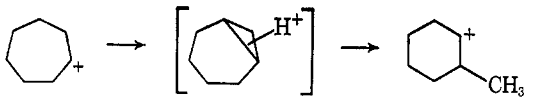
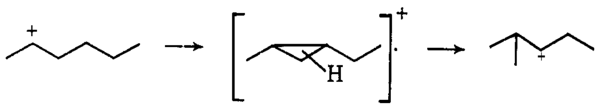
or less which suggests that hydride transfer from the naphthene to either secondary or tertiary ions is facile. It should be noted that, if the *n*-paraffins also had half-lives of this magnitude, essentially no broadening would have been detected with them.

Rearrangement of cycloheptane presumably occurs through a protonated cyclopropane intermediate or transition state without the formation of a primary ion (eq 3). A similar mechanism can be written for secondary hexyl ions but rearrangement in this case is relatively slow (eq 4). It is not clear if the apparent difference in reactivity of cycloheptane and the *n*-paraffins is due primarily to a difference in ease of ion formation or in behavior of the ion once formed.



(3)



(4)

There is no obvious reason why hydride transfer from cyclopentane to cyclopentyl ions should be any more difficult than transfer from cycloheptane to a cycloheptyl or methylcyclohexyl ion. Similarly there is no reason why *n*-butane or *n*-hexane should be reacting at much different rates than the cycloparaffins. Thus it is likely that the half-lives for all of these compounds are similar and of the order of minutes. If this is so, then the slow isomerization of *n*-butane, *n*-pentane, and *n*-hexane ought to be attributed to a relatively high activation energy for rearrangement of the secondary ion.

The behavior of secondary ion precursors may consequently be explained by assuming that (a) it is difficult to generate secondary cations whose steady-state concentration is appreciably lower than that of tertiary ions obtained from branched paraffins and that (b) branching of the secondary ion has a high energy barrier. The intermediacy of secondary ions is best seen by examining systems where rearrangement to a tertiary cation can take place easily. Such systems are found with large cycloparaffins. It is not obvious why larger barriers exist for the rearrangement of *s*-alkyl ions but the rearrangement of *n*-paraffins is generally slow. A tentative reason for this may be that the alkyl cations rearrange through the intermediacy of protonated cyclopropanes whose formation requires a relatively free cation. The cation–anion interaction in this solvent may be sufficiently strong to prevent the rearrangement unless the cation is predisposed to cyclize. Such a situation is favored where a secondary ion is generated on a naphthene since cyclization is favored by the relatively rigid framework and is subject to little steric interference by either an anion or solvent.

In summary it has been found that long-chain hydride-transfer reactions between paraffins containing tertiary C–H bonds and tertiary cations occur readily over a water-promoted aluminum bromide catalyst in 1,2,4-trichlorobenzene. The ions may undergo rapid intramolecular rearrangements which do not lead to a change in the degree of branching. Normal paraffins and naphthenes generally react more slowly, although naphthenes which can rearrange to more stable products do so easily.

Registry No.—Aluminum bromide, 7727-15-3; 1,2,4-trichlorobenzene, 120-82-1.

Anodic Oxidations. V. The Kolbe Oxidation of Phenylacetic Acid and 1-Methylcyclohexaneacetic Acid at Platinum and at Carbon

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The Kolbe oxidations of phenylacetic acid and 1-methylcyclohexaneacetic acid have been studied at both platinum and carbon anodes. At platinum, the products are derived from both free-radical and cationic intermediates, with products resulting from free radicals predominating. At a carbon anode, almost all of the products result from the generation of carbonium ions at the electrode. It is suggested that this unique ability of a carbon anode to promote the generation of carbonium ions is due to the presence within carbon of paramagnetic centers which bind the initially formed radicals, impede their desorption, and, therefore, promote a second electron transfer.

The remarkable effect on the product composition in the Kolbe reaction that results from substituting a carbon anode for the usual platinum electrode was first reported by Koehl.[1] In the case of acetate oxidation, for example, the anodic products are ethane and carbon dioxide on platinum, but almost entirely methyl acetate on carbon. The product composition in this Kolbe oxidation, as well as in others that have been studied,[1] has been rationalized by assuming that, except for special substrates where the greater stability of the carbonium ion compared with its related free radical affords driving force for a second electron transfer,[2] the predominant reaction mode on platinum is a one-electron transfer to give free-radical, product-forming intermediates. On carbon, on the other hand, the preferred reaction path appears to be a two-electron transfer at the anode to give cationic, product-forming intermediates.

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[1] W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **86**, 4686 (1964).

[2] E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanora, Jr., and E. J. Kaiser, *ibid.*, **82**, 2645 (1960); E. J. Corey and J. Casanova, Jr., *ibid.*, **85**, 165 (1963).

This distinction between carbon and platinum electrodes is also observed in more complex anodic oxidations. In the oxidation of cyclooctatetraene in acetic acid containing acetate ion,[3] the methyl-substituted products, which are obtained on platinum and which must result from methyl radicals generated at the anode, are not found with a carbon electrode. We have previously suggested[4] that the significant difference between platinum and carbon anodes may reside principally in the fact that the latter contain numerous paramagnetic centers which strongly attach any radicals formed, present a barrier to their desorption, and thus promote further oxidation to carbonium ions.

In the present investigation, evidence in support of this hypothesis has been sought by studying the Kolbe oxidation of phenylacetic acid and 1-methylcyclohexaneacetic acid on both platinum and carbon anodes. As will be elaborated subsequently, the results also have some bearing on the still controversial question of whether the free radicals generated at the anode are transformed into products while still adsorbed on the electrode[5] or after desorption from the electrode into the solution.[6]

Results

The Kolbe reactions of the two acids chosen for investigation, phenylacetic acid and 1-methylcyclohexaneacetic acid, have both been studied previously, but only with platinum anodes. Phenylacetic acid was oxidized electrochemically, first in methanol and pyridine by Fichter and Stenzl,[7] and later in methanol alone by Linstead, Shephard, and Weedon.[8] In both studies, the major product, formed in yields of approximately 50%, was bibenzyl, the normal Kolbe product resulting from coupling of benzyl radicals. This reaction is of particular interest because the intermediate benzyl radical has a relatively low ionization potential (7.76 eV),[9] and it seems relatively certain that the potential required to oxidize phenylacetic acid would be more than high enough to effect the further oxidation of a benzyl radical to a benzyl cation.

The anodic oxidation of 1-methylcyclohexaneacetic acid was first studied in methanol solution by Muhs.[10] The major product was the Kolbe dimer, 1,2-bis(1-methylcyclohexyl)ethane, obtained in 58% yield. Also obtained were 1-methylcycloheptene (11%) and 1-methyl-1-methoxycycloheptane (13%), two products in which the carbon skeleton has been rearranged and which almost certainly involve cationic precursors.

In the present investigation, the anodic oxidation of phenylacetic acid was studied in methanol, in 67% methanol–33% pyridine (by volume), and in 67% water–33% pyridine (by volume). In each experiment, 0.1 mol of substrate in 150 ml of solvent was oxidized, and 2 ± 0.2 equiv of charge/mol of phenylacetic acid was passed through the solution. In the oxidations in methanol and 67% methanol–33% pyridine, 0.5 g of sodium was used to partially convert the acid to its sodium salt, and the current was maintained at 2.0 A in methanol and at 1.0 A in 67% methanol–33% pyridine during the electrolysis. In 67% water–33% pyridine, it was not necessary to partially convert the acid to its sodium salt to obtain sufficient conductivity, and these solutions were electrolyzed at 2.0 A. In the absence of pyridine, the anode becomes coated and must be cleaned periodically. The addition of pyridine obviates this difficulty and permits the entire electrolysis to be run without interruption for electrode cleaning.

The products obtained in these oxidations are listed in Tables I–III. Only bibenzyl and toluene are clearly formed from benzyl radicals generated at the anode. The origin of methyl phenylacetate is uncertain. In a control experiment, an electrolysis solution in methanol left standing at room temperature for 24 hr without voltage applied was found to contain 0.094 g (0.00063 mol) of the ester by vpc. Such esterification would only account for a small part of the methyl phenylacetate found on electrolysis in methanol and is a much less probable reaction in 67% methanol–33% pyridine. It is an intriguing but unproven possibility that the ester arises, at least in part, from anodic oxidation of molecu-

Table I

Products Obtained on Anodic Oxidation of 0.1 Mol of Phenylacetic Acid in Methanol

Product	Moles at Pt	Moles at C
Bibenzyl	0.0132	0.0047
Benzyl methyl ether	0.0151	0.0278
Toluene	0.00065	0.00033
Benzaldehyde dimethylacetal	0.00066	0.0014
Methyl phenylacetate	0.0028	0.0048
Benzyl alcohol	0.0024	0.0041

Table II

Products Obtained on Anodic Oxidation of 0.1 Mol of Phenylacetic Acid in 67% Methanol–3% Pyridine

Product	Moles at Pt	Moles at C
Bibenzyl	0.0162	0.0000
Benzyl methyl ether	0.0135	0.0405
Toluene	0.00044	0.00040
Methyl phenylacetate	0.0036	0.0050
Benzyl alcohol	0.0036	0.0060
Phenylacetic acid (recovered)	0.0022	0.0012

Table III

Products Obtained on Anodic Oxidation of 0.1 Mol of Phenylacetic Acid in 67% Water–33% Pyridine

Product	Moles at Pt	Moles at C
Bibenzyl	0.0068	0.0000
Benzyl alcohol	0.0104	0.0240
Benzaldehyde	0.0075	0.0018
Toluene	0.0004	0.0000

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[3] L. Eberson, K. Nyberg, M. Finkelstein, R. C. Petersen, S. D. Ross, and J. J. Uebel, *J. Org. Chem.*, **32**, 16 (1967).

[4] S. D. Ross, *Trans. N. Y. Acad. Sci.*, **30**, 901 (1968).

[5] B. E. Conway and A. K. Vijh, *Electrochim. Acta*, **12**, 102 (1967); *Z. Anal. Chem.*, **224**, 149, 160 (1967).

[6] L. Eberson. *Acta Chem. Scand.*, **17**, 2004 (1963); *Electrochim. Acta.*, **12**, 1473 (1967).

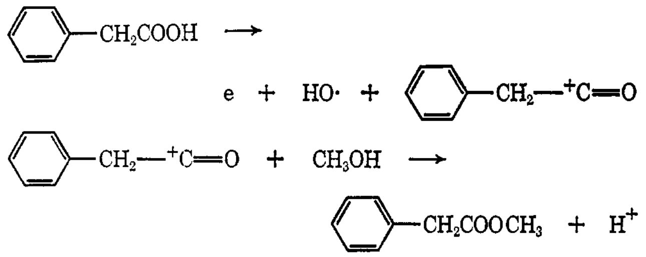
[7] Fr. Fichter and H. Stenzl, *Helv. Chim. Acta*, **22**, 976 (1939).

[8] R. P. Linstead, B. R. Shephard, and B. C. L. Weedon, *J. Chem. Soc.*, 3624 (1952).

[9] A. G. Harrison, P. Kebarle and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 777 (1961).

[10] M. A. Muhs, Ph.D. Thesis, University of Washington, 1954; *Dissertation Abstr.*, **14**, 765 (1954).

lar phenylacetic acid and involves an acylium ion as an intermediate, as shown below. All other products are best rationalized as primary products resulting from benzyl cations or as secondary products formed by further oxidation of these primary products.



In all three solvents, the anodic oxidations are accompanied by extensive tar formation. The products observed on both platinum and carbon anodes with methanol as solvent account for 48% of the starting acid. In 67% methanol–33% pyridine, 56% of the starting acid is accounted for with a platinum anode and 52% with the carbon electrode. In 67% water–33% pyridine, the conversion to identifiable products is very much lower, 32% on platinum and 26% on carbon.

A more significant distinction becomes apparent when the observed products are divided, in each case, into those resulting from free-radical intermediates and those derived from carbonium-ion intermediates. Table IV tabulates the ratios, moles of free-radical products/moles of ionic products, for each experiment. In this work, the observed number of moles of bibenzyl has in every case been multiplied by two, as this product results from the coupling of two benzyl radicals. It is clear from Table IV that, compared with a platinum anode, a carbon anode strongly suppresses or eliminates those products which result from radical intermediates.

TABLE IV

RELATIVE AMOUNTS OF FREE-RADICAL AND IONIC PRODUCTS ON THE ELECTROCHEMICAL OXIDATION OF PHENYLACETIC ACID

Solvent	Anode	Moles of free-radical products/moles of ionic products
Methanol	Pt	1.3
Methanol	C	0.26
67% Methanol–33% pyridine	Pt	1.4
67% Methanol–33% pyridine	C	0.0076
67% Water–33% pyridine	Pt	0.78
67% Water–33% pyridine	C	0.00

The Kolbe oxidation of 1-methylcyclohexaneacetic acid was studied in 67% methanol–33% pyridine at both platinum and carbon anodes. In these experiments, 0.1 mol of the acid in 150 ml of solvent was oxidized at a constant current of 1 A until 2 ± 0.1 equiv of charge had passed through the solution. Before electrolysis, the acid in these solutions was partially converted to its sodium salt with 0.5 g of sodium.

The availability of vpc has made it possible to determine some of the minor as well as the major products formed in these reactions. All of these products are shown in Table V. The 1,2-bis(1-methylcyclohexyl)ethane and the 1,1-dimethylcyclohexane result from the generation of 1-methylcyclohexylmethyl radicals at the anode. Methyl 1-methylcyclohexaneacetate may, as in the formation of methyl phenylacetate from phenylacetic acid, be the result of anodic oxidation of the acid to give the corresponding acylium ion. The remaining observed products are best interpreted as resulting from the generation at the anode of the 1-methylcyclohexylmethyl cation, and the spectrum of the found products, both with rearranged and unrearranged carbon skeletons, is typical of carbonium-ion reactions. Since spiro[2.5]octane is a possible product from this carbonium ion, particularly if the ion is present in an unsolvated or "hot" state, it was prepared independently, and its presence was sought in the electrolysis product. However, it was not present in detectable amount.

TABLE V

PRODUCTS OBTAINED ON ANODIC OXIDATION OF 0.1 MOL OF 1-METHYLCYCLOHEXANEACETIC ACID IN 67% METHANOL–33% PYRIDINE

Product	Moles at Pt	Moles at C
1,2-Bis(1-methylcyclohexyl)ethane	0.0204	0.00067
1-Methylcycloheptene and/or 1-ethylcyclohexene[a]	0.00681	0.0276
1-Methyl-1-methoxycycloheptane	0.00474	0.0214
1-Ethyl-1-methoxycyclohexane	0.00294	0.0121
Methyl 1-methylcyclohexaneacetate	0.00025	0.0000
1,1-Dimethylcyclohexane	0.00062	0.00018
1-Methyl-1-methoxymethylcyclohexane	0.0000	0.00021
1-Methylcyclohexaneacetic acid (recovered)	0.0286	0.0069

[a] Not separated by vpc.

In these reactions, tar formation was much less extensive, and it was possible to account for 77% of the starting acid with the platinum electrode and 67% of the starting acid with the carbon anode. At the platinum electrode, 74% of the observed products are formed from radical intermediates and 26% are from ionic precursors. At carbon, only 2% of the products result from free radicals, and 98% have their origin in carbonium ions. In this system, too, the carbon electrode shows a remarkable ability to divert the Kolbe reaction from its normal, preferred free-radical path and favors the generation of cationic intermediates.

Experimental Section

Materials and Reference Compounds.—The following compounds were prepared by procedures given by Muhs.[10]

1-Methylcyclohexaneacetic acid: bp 65–70° (0.04 mm); n^{23}D 1.4682.

Methyl-1-methylcyclohexylmethyl ether: bp 39–40° (30 mm); n^{23}D 1.4408.

Methyl-1-methylcyclohexaneacetate: bp 86–91° (13 mm); n^{24}D 1.4507.

Methyl 1-ethylcyclohexyl ether: bp 72–80° (35 mm); n^{25}D 1.4462.

Methyl 1-methylcycloheptyl ether: bp 60–61° (14 mm); n^{26}D 1.4507. This structure was confirmed by nmr, which showed three peaks with area ratios of 3.06:12.4:2.99.

1,1-Dimethylcyclohexane and 1-methylcycloheptene were obtained from the Aldrich Chemical Co.

1,2-Bis(1-methylcyclohexyl)ethane was isolated by distillation from a Kolbe oxidation of 1-methylcyclohexaneacetic acid in methanol: bp 73–75° (0.06 mm); n^{23}D 1.4796. The nmr spectrum showed three peaks with area ratios of 10.7:1.95:2.85.

1-Methylcyclohexanemethanol, bp 75–77° (14 mm), n^{19}D 1.4683, was prepared by the lithium aluminum hydride reduction of 1-methylcyclohexanecarboxylic acid, prepared according to Baumgarten, Bower, and Okamoto.[11]

Spiro[2.5]octane, $n^{24}\mathrm{D}$ 1.4458, was prepared from bis(bromomethyl)cyclohexane[12] by the procedure of Boord, *et al.*[13] The diol required for the above dibromide preparation was made by the method of Bergson and Biezais.[14]

Electrolyses.—The electrolysis cell and electrode assemblies are those previously described and used in the electrochemical oxidation of cyclooctatetraene at constant current.[3] The following two procedures, one with phenylacetic acid and one with 1-methylcyclohexaneacetic acid, are typical of those used.

Electrolysis of Phenylacetic Acid in 67% Methanol–33% Pyridine.—Sodium (0.5 g) was allowed to react with methanol (100 ml), and pyridine (50 ml) and phenylacetic acid (13.6 g, 0.1 mol) were added to this solution. The electrolysis, in this case with a platinum anode, was at a constant current of 1 A until 18,600 C of charge had passed through the solution. The crude electrolysis mixture was taken up in water (750 ml) and extracted with four 250-ml portions of ether. The combined ether extracts were extracted first with a solution of potassium hydroxide (6 g) in water (150 ml), then in three portions with a solution of concentrated hydrochloric acid (50 ml) in water (250 ml), and finally with water. The ether solution was dried over anhydrous magnesium sulfate and then concentrated to a volume of 50 ml for analysis by vpc.

The combined aqueous layers were made strongly acidic and extracted with two 250-ml portions of ether. The ether extract was dried over magnesium sulfate, the solvent was removed at the water pump, and the crude product was crystallized from hexane, yielding 0.3 g of recovered phenylacetic acid.

Electrolysis of 1-Methylcyclohexaneacetic Acid in 67% Methanol–33% Pyridine at a Platinum Anode.—Sodium (0.5 g) was allowed to react with methanol (100 ml). Pyridine (50 ml) and 1-methylcyclohexaneacetic acid (15.6 g, 0.1 mol) were added, and the solution was electrolyzed at 1.0 A until 21,400 C of charge had passed through the solution. The electrolysis mixture was poured into water (1 l.), and, after addition of salt, was extracted four times with a total of 1 l. of ether. The ether solution was extracted twice with 200-ml portions of hydrochloric acid (160 ml of concentrated acid in 250 ml of water), then with water, then with two 100-ml portions of 10% sodium hydroxide solution, and finally with water again. The ether solution was dried over anhydrous magnesium sulfate and concentrated to 50 ml for analysis by vpc.

All of the aqueous extracts were combined, giving a strongly acidic solution. This was extracted twice with 200-ml portions of benzene. The benzene solution was dried, and the benzene was removed at the water pump. The residue was converted to the methyl ester *via* the acid chloride, and this was analyzed by vpc as a measure of unreacted 1-methylcyclohexaneacetic acid.

Analysis by Vpc.—All of the vpc analyses were carried out with a Perkin-Elmer Model 154B vapor fractometer using helium as the carrier gas. All of the products formed in the oxidation of phenylacetic acid as well as the 1,2-bis(1-methylcyclohexyl)ethane and the methyl 1-methylcyclohexaneacetate were determined with a Perkin-Elmer large-diameter Golay column (0.06 in. × 300 ft) in which the stationary phase was Ucon polyglycol LB-550-X. The remaining products were determined on a Perkin-Elmer A column, 2 m in length, in which the solid support is diatomaceous earth and the liquid substrate is diisodecyl phthalate. In all cases, the unknown solutions were compared with standards prepared from the identified components.

Isolation of Bibenzyl.—The ether solution of the products from the oxidation of phenylacetic acid in 67% methanol–33% pyridine at a platinum anode was distilled at the water pump, with the heat supplied by a bath at 85°, to remove volatile substances. The residue was dissolved in hexane, and the bibenzyl was isolated by column chromatography. The yield was 2.51 g, mp 49–50.5° after crystallization from methanol. Analysis by vpc of this same ether solution had indicated the presence of 2.96 g of bibenzyl.

Isolation of Methyl 1-Ethylcyclohexyl Ether.—The ether solution of products from the electrolysis of 1-methylcyclohexaneacetic acid at a carbon anode was separated on a Model A-700 Aerograph Autoprep fitted with a column 20 ft × $^3/_8$ in., packed with 30% SE-30 on 45–60 Chromosorb W. The temperature was 200°. The substance separated had $n^{23.5}\mathrm{D}$ 1.4506 and was shown to be pure by analytical vpc on the Golay column, where it had the same retention time as authentic methyl 1-ethylcyclohexyl ether.

Discussion

The differences in the course of the Kolbe reaction on platinum and on carbon anodes are large and significant. At platinum, both free radicals and carbonium ions are generated, but the preferred reaction path is one in which the products result from the former type of intermediate. On a carbon anode, the latter type of intermediate is strongly favored, the formation of products attributable to free-radical intermediates is largely suppressed, and the yields of Kolbe coupling products are very low.

The present results with both phenylacetic acid and 1-methylcyclohexaneacetic acid are fully in accord with the above generalizations. They are also completely consistent with our previous suggestion[4] that the unique characteristic of a carbon electrode is the presence within it of numerous paramagnetic centers which bind anodically generated free radicals, impede their desorption into the solution, and, therefore, promote a second electron transfer to give a carbonium ion. The presence of such paramagnetic centers in carbons and graphites is well documented.[15] For an anodically formed radical, *e.g.*, $CH_3\cdot$, chemisorbed on the electrode, M, through an M–CH_3 bond, it can be shown that the M–CH_3 bond energy, as calculated by Pauling's procedure, is not significantly different when M is platinum or carbon, if one neglects the presence of paramagnetic centers on carbon.[16] It is, therefore, reasonable and even probable that the striking differences observed with carbon and platinum electrodes are due to the presence of paramagnetic centers in the former.

If one adopts Conway's hypothesis,[5] the first step in the reaction on platinum is a one-electron transfer at the anode to give a radical adsorbed on the electrode. The radical thus generated may react with another adsorbed radical to give the coupling product, or with another appropriate molecule in a hydrogen-transfer reaction (*e.g.*, to form toluene from the benzyl radical), with both reactions occurring while the radicals are still adsorbed on the electrode. Alternatively, the radical may transfer a second electron to the electrode to give a cation which will be driven from the anode by electrostatic forces and will react in the solution. The partitioning of the final products into free-radical products and carbonium-ion products will be determined by this competition, largely one of radical dimerization on the electrode surface *vs.* a second electron transfer. In accordance with the above, the different results observed on a carbon electrode might be attributed to the fact that the paramagnetic centers on carbon bind the initially generated radicals more strongly, make the radical dimerization reaction energetically more unfavorable, and, thus, promote carbonium-ion formation.

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(11) H. E. Baumgarten, F. A. Bower, and T. T. Okamoto, *J. Amer. Chem. Soc.*, **79**, 3145 (1957).

(12) E. R. Buchman, D. H. Deutsch, and G. I. Fujimoto, *ibid.*, **75**, 6228 (1953).

(13) R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **70**, 946 (1948).

(14) G. Bergson and A. Biezais, *Arkiv Kemi*, **22** (35) 475 (1964); *Chem. Abstr.*, **63**, 6996 (1965).

(15) See D. J. E. Ingram in "Chemisorption," W. E. Garner, Ed., Academic Press Inc., New York, N. Y., 1957, p 260, and references cited therein.

(16) Unpublished results by Dr. A. K. Vijh of these laboratories.

In Eberson's picture of the mechanism,[6] all of the product-forming reactions, both those involving free radicals and those involving ionic intermediates, occur in the solution. The initial step is, again, a one-electron transfer to give a radical, which may then either transfer a second electron or be desorbed from the anode surface. The product distribution will now be determined by this competition between radical desorption and electron transfer. If this view is correct, the carbon electrode favors carbonium-ion products, because the paramagnetic centers impede radical desorption and, therefore, favor electron transfer.

In the reactions now under consideration, it must be assumed that the applied potentials are sufficiently high to permit a second electron transfer from the initially generated radicals, since carbonium-ion products would not be observed on both platinum and carbon if this were not the case. If the radicals all react while adsorbed on the electrode and if the applied potential is supplying sufficient activation energy to permit a second electron transfer, it is difficult to see how radical dimerization can compete successfully with electron transfer, as it does at a platinum anode. The bimolecular, coupling reaction might be expected to have both an unfavorable enthalpy and entropy of activation. Even though the activation energy for radical dimerization in solution is normally low, in this case one must, in addition, overcome the energy by which the two radicals are held on the electrode surface. The entropy of activation might also be expected to be negative, since in addition to being detached from the electrode surface the two radicals will probably require a change in orientation with respect to the electrode before they will be able to attain a configuration suitable for coupling. The radical dimerization reaction is, moreover, a purely chemical process, and the necessary free energy of activation cannot be supplied electrochemically as it is for the electron-transfer reaction.

The Eberson picture of the Kolbe reaction obviates these difficulties. On platinum, the radicals generated are largely desorbed from the electrode, perhaps in a concerted process with elimination of carbon dioxide from an initially generated acyloxy radical. On carbon, the additional binding forces that are available attach the bulk of the radicals generated to the electrode surface, and these undergo a second electron transfer to give a cation. The present results afford some support for this interpretation even if they fall short of proving it.

Registry No.—Phenylacetic acid, 103-822; 1-methylcyclohexaneacetic acid, 14352-58-0.

Slow Rotations in Some Substituted Anilides[1]

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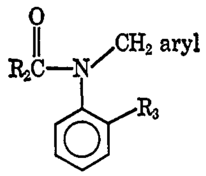
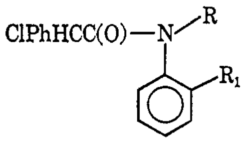
Received December 31, 1968

Barrier heights (kilocalories per mole) for rotation around the nitrogen–benzene bond are reported for 19 anilides of the type

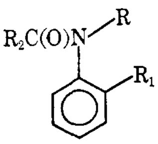


The only amide isomer observed is as shown, with the *ortho*-substituted benzene ring *trans* to oxygen (except for formanilides). However, rotation around the nitrogen–benzene bond is preceded by rotation around the carbonyl–nitrogen bond to give the activated state. Variations in barrier height from compound to compound are rationalized in terms of steric and electronic factors.

We have reported[2] the effects of various substituents, R and R_1, on the rate of rotation around the nitrogen–benzene bond in amides of the type



This paper reports a similar study of amides of the type



where R_2 and R_1 are varied and R is a benzyl (or closely related) group. Data are also included for two thioamides. The rotation rates were determined by signal shape analysis[3] of the nuclear magnetic resonance (nmr) signals (AB quartet) arising from the nonequivalent benzyl methylene protons. These protons are nonequivalent when rotation around the N–C (aromatic) bond is slow on the nmr time scale and give an AB quartet which coalesces into a singlet as rotation becomes rapid.[4-7]

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(1) The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

(2) T. H. Siddall, III, and W. E. Stewart, *J. Phys. Chem.*, in press.

(3) J. Heidberg, J. A. Weil, G. A. Janusonis, and J. K. Anderson, *J. Chem. Phys.*, **41**, 1033 (1964).

(4) T. H. Siddall, III, and C. A. Prohaska, *J. Amer. Chem. Soc.*, **88**, 1172 (1966).

(5) T. H. Siddall, III, *J. Org. Chem.*, **31**, 3719 (1966).

(6) B. J. Price, J. A. Eggleston, and I. O. Sutherland, *J. Chem. Soc.*, *B* 922 (1967).

(7) Y. Shvo, E. C. Taylor, K. Mislow, and M. Raban, *J. Amer. Chem. Soc.*, **89**, 4910 (1967).