Table IV. Bond Lengths and Angles

Atoms	Bond length, A Obsd	Temp corrected	Atoms	Angle, deg
C(1)-C(2)	1.562	1.567	C(2)-C(1)-C(2′)	90.5
C(1)-C(2′)	1.548	1.552	C(2)-C(1)-C(3)	113.7
C(1)-C(3)	1.494	1.494	C(2′)-C(1)-C(3)	116.2
C(3)-O(1)	1.315	1.345	C(1)-C(3)-O(1)	124.1
C(3)-O(2)	1.214	1.238	C(1)-C(3)-O(2)	113.0
O(1)-O(2′)	2.658	2.662[a]	O(1)-C(3)-O(2)	122.9
C(1)-H(1)	1.05		H(1)-C(1)-C(2)	118
C(2)-H(2)	1.01		H(1)-C(1)-C(2′)	112
C(2)-H(3)	1.03		H(1)-C(1)-C(3)	106
O(2)-H(4)	0.81		H(2)-C(2)-C(1)	114
			H(2)-C(2)-C(1′)	116
			H(2)-C(2)-H(3)	108
			H(3)-C(2)-C(1)	116
			H(3)-C(2)-C(1′)	114
			C(3)-O(2)-H(4)	115

[a] With the correction applied assuming the two atoms to move independently, this distance becomes 2.717 A.

than 1.537 A, the average value of a C–C single bond given by Sutton.[20]

The present work represents the third structure determination of a cyclobutane derivative in which the ring is planar, not part of a condensed polycyclic system, and not involved with endo- or exocyclic unsaturation. The other two, tetracyanocyclobutane[4] and tetraphenylcyclobutane,[1,2] crystallize in the same space group ($P2_1/c$) with the ring lying on a center of symmetry. The C–C bond lengths in the rings are comparable to ours: 1.566 ± 0.015 and 1.573 ± 0.015 A for tetraphenylcyclobutane; 1.547 ± 0.002 and 1.561 ± 0.002 A for tetracyanocyclobutane. Our work thus confirms the existence of longer-than-normal C–C single bonds in simple, planar cyclobutane derivatives.

Acknowledgment. This work was supported by the National Science Foundation under Grant GP-4550. We are indebted to Professor K. N. Trueblood for bringing this problem to our attention.

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γ Radiolysis of Cystine in Aqueous Solution. Dose-Rate Effects and a Proposed Mechanism[1]

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Abstract: Solutions of L-cystine (CySSCy) in water (3×10^{-4} *M*) were exposed to 10,000 rads of Co^{60} γ rays. *G* values were determined for the following products: $CySO_2H$, $CySO_3H$, $CySO_2SH$, $CySSO_3H$, CySH, and CySSSCy. The effect of OH and e_{aq}^- scavengers on the yields was also investigated. The yields of $CySO_2H$, $CySO_3H$, and CySH were dose-rate dependent in the range 1 to 800 rads/min. A mechanism for the radiolysis is presented and discussed: CySOH appears to be the main precursor of both $CySO_2H$ and $CySO_3H$ with O_2^- participating in formation of the latter. CySSSCy, the yield of which was independent of dose rate, is probably produced from cystine by reaction with CyS radicals.

The disulfide bond of cystine, which is essential to the tertiary structure of many enzymes and proteins, is particularly sensitive to ionizing radiation. Eldjarn and Pihl[2] have postulated that the cysteine and cystine residues of proteins form mixed disulfides with radioprotective compounds such as cysteamine. During radiolysis the protective residue reacts readily with free radicals, thereby protecting the protein.

Radiolysis of cysteine, which is also a radioprotective compound, has been subjected to detailed study recently.[3] Aqueous solutions of cystine have been investigated by several workers,[4] but many of the early studies involved high doses. The following products were identified by Markakis and Tappel:[4d] cysteine, H_2S, sulfur, sulfate, ammonia, and alanine. A detailed analysis of the initial products was first achieved by Grant, *et al.*,[5] using paper chromatography and electrophoresis. Similar studies were conducted by Forbes and co-workers[6] who examined both ultraviolet photolysis and radiolysis of cystine solutions. Brdička, *et al.*,[7] have also studied the radiolysis of cystine solutions using similar methods. Approximate *G* values were estimated by Grant, *et al.*,[5] by comparing the spots of products on paper chromatograms with those from standard solutions. The present study was undertaken to determine the yields more accurately and elucidate the

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mechanism of the radiolysis. Initially a flow system was used for the radiolysis, but it was discontinued when differences were observed between the flow system and stationary flask irradiations.[8]

Experimental Section

Materials. The L-cystine used for the radiolysis, MA grade from Mann Research Laboratories, was white, crystalline, and gave acceptable elementary analysis. L-Alanine, L-serine, and L-cysteine were obtained from the same source. L-Alaninesulfinic acid ($CySO_2H$) and L-cysteic acid ($CySO_3H$) were purchased from Calbiochem. Cystine disulfoxide was obtained from Light and Co., England. Fisher certified sodium formate and chloroacetic acid were used.

Sodium cysteine thiosulfurate ($CySSO_3Na$) was prepared as described by Sorbo[9] and crystallized as the hydrate.

Anal. Calcd for $C_3H_6NO_5S_2Na \cdot 1.5H_2O$: C, 14.34; H, 3.58; N, 5.58; S, 25.50. Found: C, 14.43; H, 3.78; N, 5.40; S, 25.52.

Sodium cysteine thiosulfonate ($CySO_2SNa$) was prepared by two different methods: (i) from cystine disulfoxide by reaction with H_2S[10] and (ii) by treating $CySO_2Na$ with sulfur.[11] The same product was obtained in both cases, but it could not be isolated. A variation of the latter method[12] produced the barium salt in a chromatographically pure state. **$CySSSO_3H$** was also obtained only as the barium salt[13] and was chromatographically pure. **Dialanine-trisulfide**, CySSSCy, was prepared by treating cystine S-monoxide with H_2S[14] and was isolated as white crystals, mp 201.5° dec.

Anal. Calcd for $C_6H_{12}N_2O_4S_3$: C, 26.45; H, 4.44; N, 10.29; S, 35.22. Found: C, 26.48; H, 4.38; N, 9.95; S, 35.12.

The cystine S-monoxide used was prepared by oxidizing cystine with performic acid as described Savige, *et al.*[14] The monoxide was a white powder and had a strong absorption band in the infrared at 1070 cm^{-1} characteristic of S-monoxides.

Irradiations. Solutions of L-cystine (3×10^{-4} *M*) in triply distilled water were irradiated in Pyrex glass vessels. Triply distilled water was prepared by redistilling distilled water from alkaline permanganate and then from sulfuric acid. Samples of 25 ml in 25- or 50-ml, round-bottom flasks were used throughout this study. The flasks were cleaned with hot chromic acid, rinsed well with distilled, doubly distilled, and then triply distilled water, and steamed. The dose rate for each size of flask at each position was determined with a $FeSO_4$ dosimeter solution. A Co^{60} source of approximately 100 curies was used for all irradiations except for those requiring dose rates of 1 or 10 rads/min for which a smaller Co^{60} source was employed. The total dose given was 10,000 rads in all cases except for irradiations at 1 rad/min and where otherwise stated. Solutions were deaerated by freezing, evacuating the flask, and thawing the solution. After repeating this procedure three times the flasks were sealed.

Analysis. A modified Technicon automatic analyzer was used for all amino acid determinations.[15,16] In order to determine the amount of cystine consumed during the radiolysis, 1 ml of the irradiated solution was placed on the cation-exchange column (Chromobeads) which was then eluted in the usual manner. A sample of the unirradiated solution was run for comparison. Norleucine was used as an internal standard for all runs using the cation-exchange column. Acidic products were examined by adding glutamic acid as a reference standard to the irradiated solution (25 ml) and pumping the mixture directly onto a column of anion-exchange resin (Dowex 1-X10). The column was then rinsed with water and the acids were eluted with sodium monochoroacetate solution as described previously.[15,16] Neutral and basic products were examined as follows. Norleucine was added to 25 ml of the irradiated solution and the mixture freeze dried. The residue was dissolved in 1 ml of water and centrifuged to remove undissolved cystine. The supernatant liquid was applied to the cation-exchange column in the usual manner. Thiodiglycol, 5 drops, was added to all irradiated solutions to prevent oxidation of products such as cysteine and alaninesulfinic acid during the analysis.

Results

The loss of cystine during radiolysis was difficult to measure, as the difference in concentration before and after irradiation was small. However, the values found for *G*(−CySSCy) were usually reproducible to within 0.6 unit for aerated solutions. The consumption of cystine in deaerated solutions was measured by deaerating the sample and the reference solution simultaneously in a multiple sealing flask. Errors due to freeze drying of the solution were thereby reduced. The results obtained are presented in Table I, together with the yields of the products discussed below.

Table I. *G* Values of Products and Sulfur Balance

	Aerated				Deaerated			
	10 rads/min		680 rads/min		10 rads/min		680 rads/min	
	G	Sulfur	*G*	Sulfur	*G*	Sulfur	*G*	Sulfur
$CySO_2H$	1.7	1.7	0.9	0.9	0.3	0.3	1.2	1.2
$CySO_3H$	0.7	0.7	1.2	1.2	0	0	0	0
CySH	0	0	0.7	0.7	0.4	0.4	2.5	2.5
CySSSCy	0.4	1.2	0.6	1.8	1.0	3.0	1.0	3.0
$CySSO_3H$	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2
$CySO_2SH$	0.05	0.1	0.05	0.1	0.05	0.1	0.05	0.1
Total S in products	...	3.9	...	4.9	...	4.0	...	7.0
CySSCy used up	2.0	4.0	2.6	5.2	1.3	2.6	2.8	5.6

The principle oxidation products in aerated solution were $CySO_2H$ and $CySO_3H$, the yields of which were reproducible to within 0.1 unit. In deaerated solutions, $CySO_3H$ was produced only in trace amounts. CySH was found in both aerated and deaerated solutions and the yields were usually reproducible to ±0.2. The trisulfide, CySSSCy, was produced in significant quantities in both aerated and deaerated solutions with *G* values reproducible to ±0.1. $CySSO_3H$ and $CySO_2SH$ were minor products and the yields given are approximate estimates. Traces of alanine and serine may also have been produced but the *G* values could not have been greater than 0.05. Small amounts of other products were present but not identified. The acid, $CySSSO_3H$, the mixed disulfide of cysteine and β-mercaptopropionic acid (deaminated cystine), and that of cysteine and cysteamine (decarboxylated cystine) were not detected in the irradiated solutions. The presence or absence of the above compounds was confirmed by comparing synthetic samples with the products in the irradiated solutions using the amino acid analyzer. The products found have all been identified previously in irradiated solutions of cystine by paper chromatography and electrophoresis.

In Table I the yields are also given in terms of sulfur atoms. In deaerated solutions, the sulfur in the products appears to exceed the sulfur in the cystine consumed. This results from difficulties in determining *G*(−CySSCy). Also, CySH oxidizes readily to CySSCy, and *G*(CySH) was slightly variable. However, despite

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Table II. Yields for Aerated Solutions of Cystine with Formate or Monochloroacetate Added

	770 rads/min Formate (M)			770 rads/min Chloroacetate (M)			10 rads/min Chloroacetate (M)		
	10^{-4}	10^{-3}	10^{-2}	10^{-4}	10^{-3}	10^{-2}	10^{-4}	10^{-3}	10^{-2}
$G(CySO_2H)$	0.5	0.25	0.15	0.6	0.7	0.8	1.3	1.1	0.9
$G(CySO_3H)$	0.95	0.65	0.15	1.15	0.8	0.3	0.4	0.4	0.3
G(CySSSCy)	0.35	0.2	0.15	0.4	0.5	0.4	...	...	...

this difficulty it is evident that most of the sulfur is accounted for.

Yields of $CySO_2H$ and $CySO_3H$ in aerated solutions were determined at several dose rates by irradiating at various distances from the sources. The results are illustrated in Figure 1a. Each point on the graph is the mean of two determinations which agreed to within 0.1 unit. During the irradiation the pH changed from 5.6 to 4.6. The yields of $CySO_2H$ at different dose rates in deaerated solutions are shown in Figure 1b. The results there were less reproducible, but the cause of the variation was not discovered. The lowest dose rate studied was 1 rad/min in both cases, *i.e.*, Figure 1a and b, for which a total dose of 7500 rads was used.

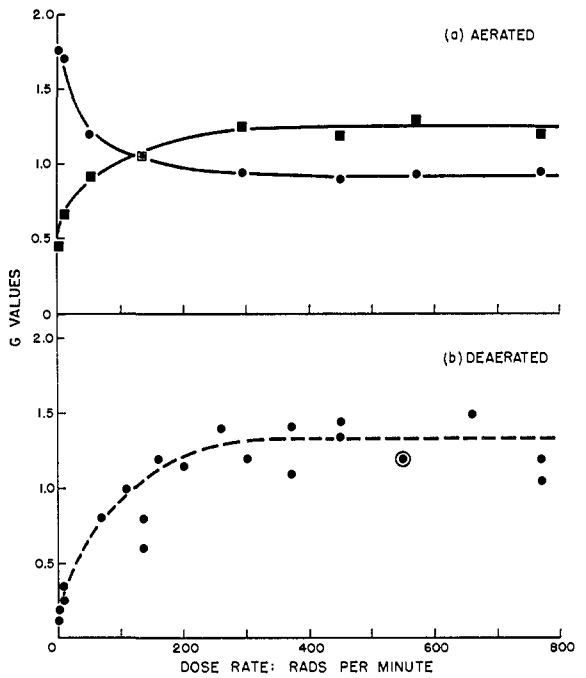

Figure 1. Variation of G values with dose rate for $CySO_2H$ (●) and $CySO_3H$ (■): (a) aerated solution; (b) deaerated solution.

The effect of reducing the total dose was examined using aerated solutions at a dose rate of 760 rads/min. The yields of CySH, CySSSCy, $CySO_2H$, and $CySO_3H$ were determined after exposure to 10,000, 8000, 6000, and 4000 rads. The G values for all four products did not vary from the results in Table I (680 rads/min). The yields of $CySO_2H$ and $CySO_3H$, which could be measured more accurately, were also determined after irradiation with 2000, 1000, and 500 rads, using samples of 50, 75, and 100 ml, respectively. There was still no measurable change in G values although, of course, the experimental error was greater at these low doses.

Aerated cystine solutions were also irradiated after addition of sodium formate. The rate of reaction of formate ions with OH radicals is very high,[17,18] but it reacts only slowly with e_{aq}^-. G values were determined for $CySO_2H$, $CySO_3H$, and CySSSCy at three different concentrations of sodium formate, and the results are given in Table II. The concentration of cystine was kept at 3×10^{-4} M in all cases. The yields for irradiation of cystine in water (unbuffered), determined at the same time, were $G(CySO_2H) = 0.75$ and $G(CySO_3H) = 1.2$. Although the yields for aerated solutions were reproducible at any given time, a slight variation was observed when they were determined at different times of the year. This may be due to changes in the temperature of the water in the irradiation well. In order to scavenge only the hydrated electron during radiolysis, monochloroacetate ions were used.[17,18] Aerated cystine solutions with sodium monochloroacetate added were irradiated in the usual way, and the G values obtained are also listed in Table II.

Some irradiations were performed with formate or monochloroacetate ions present in deaerated solutions. At 770 rads/min addition of formate ions (10^{-3} M) reduced the yield of $CySO_2H$ from $G = 0.75$ to $G = 0.4$. Simultaneously, $CySO_3H$, which normally occurs only in trace amounts in deaerated solutions, was produced in measurable yield, $G = 0.5$. The presence of monochloroacetate ions (10^{-3} M) increased the yield of $CySO_2H$ from $G = 0.3$ to $G = 0.55$ at 10 rads/min. When the monochloroacetate concentration was raised to 10^{-2} M, $G(CySO_2H)$ rose to 0.8 at this dose rate.

Discussion

From the results in both aerated and deaerated solutions, the following general conclusions can be drawn. (i) Oxygen is necessary for production of $CySO_3H$ from cystine by radiolysis. (ii) The decrease in $CySO_3H$ at low dose rates is approximately equal to the increase in $CySO_2H$ which suggests that they come from the same intermediates. (iii) Since the yield of $CySO_2H$ is small at low dose rates in deaerated solutions and large at low dose rates in aerated solutions, oxygen appears to be necessary for its production at low dose rates. (iv) Variation of the yields with dose rate suggests that some of the initial products are either stable free radicals, which participate in secondary radical reactions, or unstable compounds, which decompose or react with radicals.

Several schemes have been proposed to explain the radiolysis of cystine and related disulfides,[5-7,19] and some of the reactions suggested are included in the present mechanism. This mechanism offers a general explana-

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tion of the radiolysis with respect to the major products. Other reactions may occur and some of the reactions presented here may have to be modified when more information becomes available. It is assumed that active radicals (OH and e_{aq}^-) and H_2O_2, etc., are produced from water in the accepted way. In aerated solutions, the initial reaction appears to be

$$CySSCy + OH \longrightarrow CySOH + CyS \quad (1)$$

The sulfenic acid produced in reaction 1 is unstable and may react in various ways.

$$CySOH + O_2^- \longrightarrow CySO_3^- + H \quad (2)$$

$$CySOH + CySOH \longrightarrow CySO_2H + CySH \quad (3)$$

$$CySOH + H_2O_2 \longrightarrow CySO_2H + H_2O \quad (4)$$

A radical, identified as CyS, has been detected in aqueous solution by Armstrong using esr spectroscopy.[20] It was obtained by reacting OH radicals, produced from $TiCl_3$ and H_2O_2, with cystine or cysteine in a flow system and was relatively unstable. The CyS radical produced in reaction 1 may combine with another CyS radical or with oxygen to yield $CySO_2$. Radicals of this type (*i.e.*, RSO_2) have been reported to be stable at room temperature.[21] Thus it is reasonable to assume that $CySO_2$ is sufficiently stable in aqueous solution to participate in secondary reactions, *e.g.*

$$CySO_2 + CyS \longrightarrow CySO_2SCy \quad (5)$$

$$CySO_2 + CySO_2 \longrightarrow CySO_2SO_2Cy \quad (6)$$

$$CySO_2SO_2Cy + H_2O \longrightarrow CySO_2H + CySO_3H \quad (7)$$

The S,S-dioxide produced in reaction 5 has been detected in acidic solutions[5] but is unstable at pH 5 and decomposes as follows.

$$CySO_2SCy + H_2O \longrightarrow CySO_2H + CySOH \quad (8)$$

As indicated in reactions 1 to 8, the main oxidation products, $CySO_2H$ and $CySO_3H$, can be formed from the same intermediates by different reactions. Variation of the dose rate could affect the competition between these reactions and consequently change the yields of these two products. Reaction 2 probably becomes less important at low dose rates, whereas reaction 4 will increase using hydrogen peroxide formed from decomposition of O_2^-.[22] In a recent review, Burns and Barker pointed out that dose-rate effects may result even at low dose rates where competition exists between two reactions of different order.[23]

The studies with formate and monochloroacetate ions present in aerated solutions substantiate the mechanism proposed. Formate ions, which compete with reaction 1 for OH radicals, reduce the yield of all products to an almost equal extent. This agrees with the suggestion that reaction 1 is the initial step in the radiolysis. Monochloroacetate ions, which react readily with e_{aq}^-, would decrease the amount of O_2^- formed and hence affect reactions 2 and 4. The over-all effect of this should be to substantially reduce the yield of $CySO_3H$ at all dose rates and reduce the yield of $CySO_2H$ at low dose rates. The results agreed with this observation. Radiolysis of cystine solution with monochloroacetate ions present decreased the yield of $CySO_3H$ but not the yield of $CySO_2H$ at high dose rates. At low dose rates the yields of both were reduced. Indeed it would appear from this that reaction 2, or some variation of it, produces most of the $CySO_3H$.

In deaerated solutions reactions 1, 3, and 4 will still occur. In addition, e_{aq}^- probably attacks cystine to give cysteine which in turn may react with the sulfenic acid.

$$CySSCy + e_{aq}^- \longrightarrow CySH + OH^- + CyS \quad (9)$$

$$CySH + CySOH \longrightarrow CySSCy + H_2O \quad (10)$$

(These reactions may also occur to some extent in aerated solutions since the reaction rates for e_{aq}^- with cystine and oxygen are similar in magnitude.[18,24]) Competition between reactions 3 and 10 may account for the dose-rate effect in deaerated solution if it is assumed that reaction 3 is much faster than reaction 10, thereby allowing it to predominate at high dose rates. The low values of $G(-CySSCy)$ and $G(CySH)$ at low dose rate support this conclusion. Further evidence for this mechanism was obtained from the experiments with monochloroacetate ions present in deaerated solutions to compete with reaction 9 for e_{aq}^-. The yields of $CySO_2H$ increased as the concentration of monochloroacetate ions increased, presumably because reaction 10 was suppressed.

In aerated solutions, formation of the trisulfide, CySSSCy, was almost independent of dose rate and monochloroacetate ions but suppressed by formate ions. Yields were higher in deaerated solutions but could be reduced by monochloroacetate ions. This indicates that only the OH radical participates in formation of CySSSCy in aerated solutions while both OH and e_{aq}^- are involved in deaerated solutions. These results can be explained readily if CySSSCy is produced by the following reaction.

$$CyS + CySSCy \longrightarrow CySSSCy + Cy \quad (11)$$

The by-product in this reaction, $CH_2CH(NH_2)COOH$, could decompose in various ways, perhaps *via* the unstable aminoacrylic acid[6] or to ammonia and acrylic acid. Ammonia was always present in the irradiated solutions, but the yields were not measured during this study.

An interesting aspect of the dose-rate effect and the products involved is that they could be related to the radioprotective property of cysteine. This property may be due to the ease of formation of the sulfonic acid derivative in aerated environments. Preliminary studies of some similar compounds in aqueous solution gave the following results. Radiolysis of homocystine was dose-rate dependent in an analogous manner and gave a yield of sulfonic acid similar to cystine. Cystamine, when examined similarly, gave a very high yield of sulfonic acid which was independent of dose rate. Penicillamine disulfide, however, gave a very low yield of sulfonic acid and the radiolysis was not dose-rate dependent. Cysteine and cysteamine are radioprotective compounds whereas penicillamine is not.[25] Some in-

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vestigators have reported that homocysteine is radioprotective,[26] while others have found it to be nonprotective.[27] Further studies of compounds of this type, including unsymmetrical disulfides, are in progress.

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Study of the Radical Anion Formation of Some Diphenylacetylenes in Dimethylformamide[1]

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Abstract: The polarographic reduction and the esr investigation of the radical anions of diphenylacetylene, *o*-, *m*-, *p*-methyldiphenylacetylenes, *p,p'*-dimethyldiphenylacetylene, *p*-methoxydiphenylacetylene, *p*-nitrodiphenylacetylene, and 1-naphthylphenylacetylene in dimethylformamide solution were carried out. The cases of the reduction of diphenylacetylene and *p*-nitrodiphenylacetylene are discussed in detail. Sufficiently intense and well-resolved esr spectra were obtained for diphenylacetylene, *p,p'*-dimethyldiphenylacetylene, and *p*-nitrodiphenylacetylene radical anions, permitting a satisfactory interpretation and assignment of the splitting constants. The Hückel and McLachlan MO methods were used to calculate the unpaired spin densities. Good agreement was obtained between experimental and calculated results.

Aromatic hydrocarbons and their derivatives in general produce relatively stable free radical anions on electrolytic reduction in aprotic solvents. It was of interest to us to extend such anion production to acetylenic compounds. A study of the literature shows that, with the exception of the work on the electrolytic reduction of diphenylacetylene reported by Wawzonek and Wearring,[2] no such investigations have been reported on other acetylenic compounds. We have therefore carried out the electrolytic reduction of a series of diphenylacetylene derivatives in dimethylformamide solution and used electron spin resonance (esr) to characterize the resulting free radical anions. With the aid of spin densities estimated from molecular orbital calculations, a reasonable interpretation of the esr spectra was realized, and experimentally consistent values of the molecular orbital integral parameters for the acetylenic bond were established.

Experimental Section

The esr spectra were recorded with a Varian spectrometer using 100-kc field modulation, a 6-in. magnet, and a variable-temperature accessory. Magnetic field measurements were made with a Harvey-Wells nmr precision gaussmeter.

The radical anions were generated inside of the resonance cavity in a manner similar to that reported by Geske and Maki.[3] The description of the cell used has been published previously.[4] A mercury cathode was used in the reductions. The potentials at which the reductions were carried out were chosen from the polarographic half-wave potentials, taking into account the potential drop calculated from the known resistance of the electrolytic cell. A solution of 0.03 *M* tetra-*n*-butylammonium iodide in dimethylformamide was used as a supporting electrolyte.

The polarographic determinations were made with a Sargent-Heyrovský polarograph. The polarographic capillary had a drop-time of 5.1 sec for an open circuit and flow rate of 1.281 mg/sec in dimethylformamide when the mercury column height was 45 cm. The half-wave potentials ($E_{1/2}$) were measured using a saturated calomel electrode (sce) as a reference. Special precautions were taken to avoid leakage of the water solution from the calomel electrode to the electrolytic cell.

The oscillopolarographic current *vs.* potential curves[5,6] at various frequencies were displayed on a Tektronix 514 AD oscilloscope. A Hewlett-Packard 202A low-frequency function generator was used as a variable frequency triangular wave source. All the polarographic measurements were made at room temperature (22°).

The dimethylformamide employed was Fisher's infrared spectranalyzed chemical grade which was further purified by drying over anhydrous potassium carbonate followed by distillation at reduced pressure (20 mm).[7] The tetra-*n*-butylammonium iodide was obtained from Eastman Kodak Co. and further purified by recrystallization. The *cis,sym*-diphenylethylene was obtained from the City Chemical Corp. The *trans,sym*-diphenylethylene and diphenylacetylene were used from an older stock and freshly recrystallized. The diphenylacetylene derivatives were prepared by the method of Stephens and Castro.[8] This method consists of heating an equal molar mixture of cuprous phenylacetylide or cuprous *p*-methylphenylacetylide with various *ortho*-, *meta*-, or *para*-substituted iodobenzenes in dry pyridine under a nitrogen atmosphere for 8 hr. The reaction mixtures are diluted with water and then extracted with ether. The crude acetylenes were recrystallized from methanol and then sublimed. The melting points were as follows: diphenylacetylene, 59.5–61.4° (reported value 59–60°); *p*-, *m*-, and *o*-methyldiphenylacetylenes, 70.9–71.8, 30.2–31.2, and 22.8–23.2°, respectively; *p,p'*-dimethyldiphenylacetylene, 138–138.7°; *p*-methoxydiphenylacetylene, 58–58.8° (reported value 58–59°). The *p*-nitro

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