Then 300 ml of 3-methylbutyn-3-ol was added with vigorous stirring under N_2 during 0.5 hr. The resulting solution was treated with 125 g of *p*-fluoronitrobenzene, added dropwise, and stirred at room temperature until 95% of the base had been consumed (3 days). It was then added to water and extracted with ether. The ethereal extract was washed with 1 *N* aqueous NaOH and then with water and dried ($MgSO_4$). Distillation gave recovered *p*-fluoronitrobenzene, bp 80–92° (10–20 mm), and 37 g of product of bp 80–90° (0.01 mm), a 35% yield.

Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40. Found: C, 64.78; H, 4.99.

Method E. Reduction of the Nitrophenyl Ether by Iron in Ethanol. 3-(4-Aminophenoxy)-3-methylbutyne.—The nitrophenoxy compound, 0.1 mol, was dissolved in 120 ml of 95% ethanol containing 4 ml of concentrated HCl, and 50 g (0.86 mol) of electrolytic iron powder was added in portions with stirring, starting immediately to minimize acid-catalyzed destruction of ether. After addition of the iron had been completed (*ca.* 15 min), the mixture was stirred another hour, 4 g of sodium acetate was added, and stirring was continued another hour. The precipitate was removed by filtration with a filtering aid and washed with ethanol. The combined filtrate and washings were concentrated *in vacuo* (aspirator and hot water bath) to ~60-ml volume and partitioned between water (1 l.) and ether (three 200-ml portions), and the ether was rapidly extracted with three 150-ml portions of 1 *N* aqueous HCl. The acidic solutions were basified with NaOH as each portion was separated and then extracted back into ether. The dried ($MgSO_4$) ethereal solutions were stripped of ether using a water bath (never over 80° for the dimethyl propargyl ether) and aspirator.

Typically with these precautions, the 3-(4-aminophenoxy)-3-methylbutyne was produced in 35% of the theoretical yield, with 96% of the theoretical acetylenic H.

Anal. Calcd for $C_{11}H_{13}NO$ (base): C, 75.43; H, 7.43; N, 8.00. Found: C, 75.43; H, 7.60; N, 8.04.

The hydrochloride was prepared in, and recrystallized from, anhydrous ethanol–ether and gave satisfactory elemental analyses.

Anal. Calcd for $C_{11}H_{14}ClNO$: C, 62.41; H, 6.67; N, 6.62. Found: C, 62.00; H, 6.65; N, 6.38.

2,2-Dimethyl-6-acetamidochroman.—Detailed preparations of this both by catalytic reduction of the chromene and by acid-catalyzed cyclization of 2-(3-methyl-2-buten-1-yl)-4-acetamidophenol will be found in British Patent 1,121,307 (1968).

Kinetics.—In general, 2.0-g samples of the ether were dissolved in 10 ml of *o*-dichlorobenzene, and the mixtures were heated when necessary in a steam bath until a homogeneous solution was formed. Then 0.2-ml aliquots were pipetted into ampoules which were flushed with N_2 for several minutes and sealed. Six to eight ampoules were placed in a Haake constant temperature bath, Model FT, containing silicone oil preheated to the selected temperature, and withdrawn singly through 6–8 half-lives, cooled to room temperature, and titrated for acetylenic hydrogen.[24] Total times of at least 4 hr and generally 1–5 days were used to minimize errors in time of cooling. Thermometers graduated to 0.2° (Brooklyn Thermometer Co.) were calibrated with Fisher triple-point standards, assuming the melting point to be identical with the triple point within the accuracy required.

Rate constants were calculated after discarding aberrant points found by manual (semilog paper) plots of log titer *vs.* $1/T_{abs}$ but never more than one point was discarded per run. The k was determined from a least-squares program, LINREG, available from the Program Library, General Electric Computer Time Sharing System, by substituting log titer for Y. All points of ln titer *vs.* time were weighted equally. Correlation coefficients better than 0.95 were regularly obtained.

The rates of thermal cyclization of the compounds 1 to give **3** directly determined are given in Table V, where R, R′, and Z refer to compound 1 structure.

Registry No.—**1a** (X = OCH_3), 17061-86-8; **1a** (X = NHAc), 26557-77-7; **1a** (X = H), 13610-02-1; **1a** (X = Cl), 19130-39-3; **1a** (X = NO_2), 17061-85-7; **1a** (X = CN), 33143-80-5; **1a** (X = NH_2), 26557-78-8; **1b** (X = OCH_3), 33146-82-7; **1b** (X = NHAc), 33143-83-8; **1b** (X = H), 1596-40-3; **1b** (X = Cl), 33143-85-0; **1b** (X = NO_2), 33143-86-1; **1b** (X = CN), 33143-87-2; **1b** (X = NH_2), 33143-88-3; **1c** (X = OCH_3), 33143-89-4; **1c** (X = NHAc), 2109-83-3; **1c** (X = H), 30504-61-1; **1c** (X = NO_2), 2109-84-4; **1c** (X = CN), 33143-92-9; **1c** (X = NH_2), 33143-93-0; **1c** HCl (X = NH_2), 33213-36-4; **3a** (X = NHAc), 33143-94-1; **3a** (X = CN), 33143-95-2; **3a** (X = NO_2), 16336-26-8; **3b** (X = OCH_3), 33143-98-5; **3b** (X = NHAc), 33143-99-6; **3b** (X = Cl), 33143-97-4; **3b** (X = NO_2), 33144-00-2; **3b** (X = CN), 33144-01-3; **3c** (X = NHAc), 19849-34-4; **3c** (X = NO_2), 33143-28-1; **3c** (X = CN), 33143-29-2.

(24) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," 3rd ed, Wiley, New York, N. Y., 1963, p 389.

Structure–Basicity Relationships of Sulfonium Ylides

K. W. RATTS

Research Department, Agricultural Division, Monsanto Company, St. Louis, Missouri 63166

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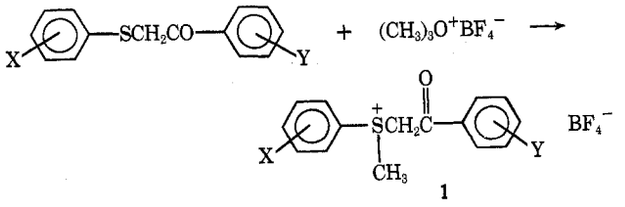
The substituent effect on basicity for a series of arylmethylphenacylsulfonium salts was determined. For the aryl substituents $\rho = +1.13$–1.23 and for the aroyl groups $\rho = +2.63$–2.68. The pK_a values for a series of dialkyl 4-bromophenacylsulfonium salts are directly related to the predicted effect of the S-attached groups on the degree of positive charge on sulfur. The results are interpreted in terms of the effect of various substituents on (1) carbanion delocalization and (2) inductive stabilization *via* the positively charged sulfur group.

The basicity of P ylides is significantly related to their nucleophilicity. A linear correlation between basicity and nucleophilicity has been observed in at least one case.[1] S ylides, however, exhibit no such correlation.[2] To outline fully the factors important to ylide basicity, an understanding of substituent effects is necessary. The purpose of this work is to define the above relationships for S ylides.

A series of methylarylphenacylsulfonium tetrafluoroborates (**1**) was prepared by alkylation of the corresponding sulfides (Table I) with trimethyloxonium tetrafluoroborate.



1

The salts and their pK_a's are listed in Table II. A

(1) S. Fliszar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, **46**, 1580 (1963).

(2) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).

TABLE I

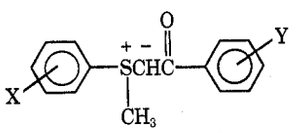
ARYL PHENACYL SULFIDES $XC_6H_4SCH_2COC_6H_4Y$

X	Y	Registry no.	Mp, °C	Yield, %	Calcd, % S	Calcd, % Hal	Calcd, % N	Found, % S	Found, % Hal	Found, % N
4-*tert*-C_4H_9	H	33191-96-7		84[a]						
4-CH_3	H	33046-45-6	36–37	75	13.23			13.30		
3-CH_3	H	27047-18-3	38–39		13.22			13.19		
H	H	16222-10-9	51–53	92	12.21	13.49		11.89	13.60	
4-Cl	H	30168-33-3	76–78	60	12.20	13.50		12.09	13.32	
4-Br	H	7312-06-3	77–78	90	10.44	26.02		10.51	25.96	
4-NO_2	H	33046-48-9	111–113	97	11.73		5.07	11.70		5.08
4-*tert*-C_4H_9	4-Cl	33191-98-9	89–90	77	10.06	11.12		9.78	11.12	
4-*tert*-C_4H_9	3-OCH_3	33191-99-0		95[a]						
4-*tert*-C_4H_9	4-OCH_3	33046-49-0	70–71	86	10.19			10.45		
H	4-Cl	33192-00-6	58.5–59.0	67	12.21	13.49		11.89	13.60	
4-Cl	4-Cl	33046-50-3	103–105	95	10.79	23.86		10.93	24.03	
4-Cl	3-OCH_3	33046-51-4		100[a]						
4-Cl	4-OCH_3	33046-52-5	72–74	92	10.96	12.11		11.38	12.68	
4-NO_2	4-Cl	33046-53-6	131–132	37	11.52	4.55		10.13[b]	5.15[b]	

[a] The crude undistilled oil obtained in these reactions was used directly in the preparation of the corresponding sulfonium salts. [b] This compound, though analyzing incorrectly for the sulfide, gave a sulfonium salt which analyzed correctly; see Table II.

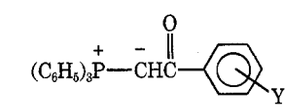
summary of $\sigma\rho$ treatment of the pK_a's is given in Table III. The pK_a values were determined by the titrimetric methods.[3]

The stabilization of the S ylides (**2**) by phenacyl-attached electron-withdrawing groups is indicated by the ρ values 2.63–2.68. This compares with values of



2a, X = 4-*tert*-C_4H_9
b, X = 4-Cl

2.3 for triphenylphosphonium phenacylides (**3**)[1], 2.1 for dimethylsulfonium phenacylides (**4**),[2] and 2.2–2.3 for pyridinium phenacylides (**5**) with Y varied.[4] Direct resonance interaction of the carbanion carbon increases the ρ value significantly, as illustrated by triphenylphosphonium fluorenylides (**6**) with Y varied (ρ = 5.0).[5]



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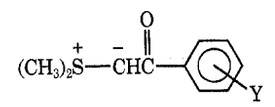

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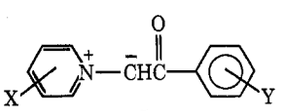

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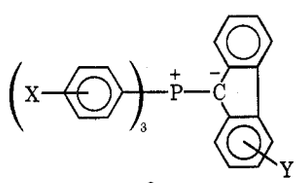
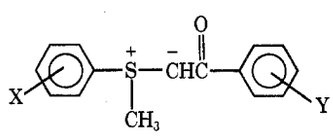


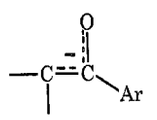
6

Stabilization of *S*-arylsulfonium ylides (**7**) by electron-withdrawing aryl substituents is indicated by the ρ values 1.13-1.23. The smaller ρ value indicates, however, less dependence of basicity upon a substituent in the *S*-aryl ring than in the phenacyl group,

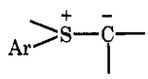


7a, Y = H
b, Y = 4-Cl

i.e., the I effect of a substituted aryl ring is greater when attached to the pπ–pπ delocalization system i



i



ii

than when attached to the dπ–pπ delocalization system ii. The same is observed in triphenylphosphonium fluorenylides (**6**) with X varied, where the ρ value is 1.7.[5] Pyridinium phenacylides[4] with X varied show a greater dependence (ρ = 2.6–3.1), but in that instance the positive heteroatom, nitrogen, is part of the resonance system directly affected by the attached group.[5] This type of stabilization is markedly dependent upon the type of carbanionic ylide considered, since $(XC_6H_5)_3P{=}NAr$ has a ρ value of 3.1.[6]

The p*K*a's of a series of *S*-alkyl substituted ylides were determined (Table IV).

Groups which stabilize the positive charge on sulfur increase the basicity of the corresponding ylide. This is evidenced by the higher values for **8** (7.4) and **13** (8.13). The stabilization involves delocalization of the positive charge by methyl[7] and transannular ring effects.[8] Such delocalization increases the extent of adjacent negative charge by reducing inductive electron withdrawal and decreasing pπ-dπ overlap with positive sulfur. Consequently, replacing *S*-methyl groups (**8**) with *S*-ethyl groups (**9**) results in a lower pK_a (7.4 → 6.46).[9] Similarly a ring compound such

(3) A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **85**, 2790 (1963). Linear regression analysis was done by computer where r = multiple correlation coefficient and s = standard error of estimate.

(4) W. G. Phillips and K. W. Ratts, *J. Org. Chem.*, **35**, 3144 (1970).

(5) A. W. Johnson, S. Y. Lee, R. A. Swor, and L. D. Ryder, *J. Amer. Chem. Soc.*, **88**, 1953 (1966).

(6) A. W. Johnson and S. C. K. Wong, *Can. J. Chem.*, **44**, 2793 (1966).

(7) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

(8) N. J. Leonard, T. W. Milligan, and T. L. Brown, *J. Amer. Chem. Soc.*, **82**, 4075 (1960).

(9) A. W. Johnson and R. T. Amel report a similar lowering of pK_a values when methyl groups are replaced by butyl groups; see ref 10.

(10) A. W. Johnson and R. T. Amel, *Can. J. Chem.*, **46**, 461 (1968).

TABLE II

X	Y	Registry no.	Mp, °C	Yield, %	Calcd, % C	H	S	Hal	N	Found, % C	H	S	Hal	N	Nmr, τ CH_3S^+	SCH_2CO	pK_a
4-*tert*-C_4H_9	H	33043-69-5	138–139	95	59.08	6.00	8.30			59.27	6.10	8.54			6.56	4.45	7.19
4-CH_3	H	33043-70-8	130–135	40	55.83	4.99	9.32			55.96	5.06	9.66			6.58	4.45	7.16
3-CH_3	H	33043-71-9	115–116	93	55.83	4.99	9.32			55.73	4.99	9.44			6.58	4.44	7.09 (7.06)
H	H																
4-Cl	H	33192-02-8	123–124	93	49.42	3.87	8.79	9.72		49.69	3.89	8.93	9.74		6.52	4.39	6.58
4-Br	H	33043-72-0	111–112	91	44.04	3.45	7.84	19.53		44.02	3.42	8.04	19.43		6.54	4.36	6.58
4-NO_2	H	33043-73-1	133–134	48	48.02	3.76	8.69		3.73	48.48	3.81	8.69		3.77	6.42	4.16	6.05
4-*tert*-C_4H_9	4-Cl	33043-74-2	158–159	35	54.24	5.27				54.41	5.30				6.59	4.50	6.62
										54.23					6.59	4.49	7.11
4-*tert*-C_4H_9	3-OCH_3	33043-75-3	91–94	49			7.7					7.45			6.59	4.49	7.11
4-*tert*-C_4H_9	4-OCH_3	33043-76-4	137–139	14			7.7					7.61			6.63	4.56	8.01
H	4-Cl	33043-77-5	155–157	94	49.41	3.87	8.79	9.72		49.85	3.61	3.73	9.80		6.56	4.44	6.44
4-Cl	4-Cl	33043-78-6	147–149	9			8.04					8.50			6.56	4.46	6.07
4-Cl	3-OCH_3	33043-79-9	94–100	13	48.7	4.09	8.13	8.98		49.02	4.13	8.37	9.22		6.56	4.41	6.61
										49.18	4.26						
4-Cl	4-OCH_3	33043-80-0	143–144	75	48.7	4.09	8.13	8.98		49.63	4.21	8.30	9.21		6.59	4.48	7.46
4-NO_2	4-Cl	33043-81-1	170–174	76	43.98	3.2		8.66		44.22	3.01		8.37		6.46	4.23	5.54

TABLE III

$\sigma\rho$ TREATMENT OF pK_a VALUES FOR SALTS 1

Substituents	Equation	r	s
Vary X, Y = H	$pK_a = 6.96 - 1.23\sigma$	0.98	0.08
Vary X, Y = 4-Cl	$pK_a = 6.40 - 1.13\sigma$	0.99	0.06
Vary Y, X = 4-*tert*-C_4H_9	$pK_a = 7.28 - 2.68\sigma$	0.98	0.12
Vary Y, X = 4-Cl	$pK_a = 6.73 - 2.63\sigma$	0.97	0.17

TABLE IV

pK_a VALUES FOR SULFONIUM 4-BROMOPHENACYLIDES

Compd	Registry no.	M^+	pK_a
8	7380-85-0	$(CH_3)_2\overset{+}{S}-$	7.4[a]
9	33046-55-8	$(C_2H_5)_2\overset{+}{S}-$	6.46
10	33046-56-9	$(CH_2)_4\overset{+}{S}-$	7.54
11	33046-57-0	$(CH_2)_5\overset{+}{S}-$	7.00
12	33046-58-1	$S(CH_2CH_2)_2\overset{+}{S}-$	6.63
13	33046-59-2	$S(CH_2)_3\overset{+}{S}-$	8.13

[a] Reference 4. [b] Kindly supplied by Professor N. J. Leonard; see J. Kleiner, Ph.D. Thesis, University of Illinois.

as **12**, where the sulfur atom is not positioned to stabilize the positive sulfur atom as it is in **13**, exhibits a lower pK_a (8.13 → 6.63).

Tieing the *S*-alkyl group into a ring tends to increase pK_a; *e.g.*, compare **9**, pK_a = 6.46, and **10**, pK_a = 7.54. Increasing the ring size lowers the pK_a value: **10**, 7.54; **11**, 7.00. Strain in the five-membered ring **10** conceivably results in increased p character in the ring C–S bonds and increased s character in the exo C–S bond, which decreases the acidity of protons attached to the exo carbon atom. Consequently, ylide **10** is more basic than ylide **9** or **11**.

The above results form a consistent picture of the structure–basicity relationships in S ylides. Electron delocalization by an attached group at any point in the molecule leads to decreased basicity. Such action by S-attached groups is related to the expected amount of sulfur positive charge. An increase in positive charge results in a stronger inductive effect, *via* increased electronegativity at sulfur, and stronger $d\pi$–$p\pi$ overlap, *via* decreased size of d orbitals to correspond more closely to p orbitals (**10**).

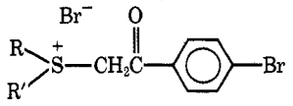
It is now possible to prepare S ylides of closely predicted basicities to determine the contribution of basicity to resulting nucleophilicities and finally reactivity.

Experimental Section

Preparation of Aryl Phenacyl Sulfides.—The procedure used is illustrated by 4′-*tert*-butylphenyl-4′-chlorophenacyl sulfide. Sodium (11.5 g, 0.5 g-atom) was dissolved in 350 ml of absolute ethanol. 4′-*tert*-butylthiophenol (83.2 g, 0.5 mol) was then added to the sodium ethoxide solution, followed by portionwise addition of 2-bromo-4′-chloroacetophenone (116.8 g, 0.5 mol). The mixture was heated at reflux for 10 min and poured onto 2 l. of ice. Filtration of the suspension gave a gummy brown solid which upon recrystallization from methanol yielded 123.3 g (77%) of 4′-*tert*-butylphenyl-4′-chlorophenacyl sulfide, mp 89–90°. The remaining sulfides prepared are listed in Table I.

Preparation of Arylmethylphenacylsulfonium Tetrafluoro-

TABLE V[a]



R	R′	Registry no.	Mp, °C	pK	Calcd, % C	Calcd, % H	Calcd, % Br	Calcd, % S	Found, % C	Found, % H	Found, % Br	Found, % S
C_2H_5	C_2H_5	6320-83-8	122–123	6.46	39.15	4.38	43.41	8.71	39.22	4.33	43.46	8.76
$-CH_2(CH_2)_2CH_2-$		19158-69-1	123–125	7.54	39.37	3.85	43.65	8.76	40.18	3.93		
$-CH_2(CH_2)_3CH_2-$		33046-62-7	141–142	7.00	41.07	4.24	42.04	8.43	40.47	4.07	42.43	8.56
$-CH_2(CH_2)_4CH_2-$		33046-63-8	149–150		42.66	4.60	40.55	8.13	42.66	4.96	40.17	7.99

[a] R = R′ = CH_3, reference 4; R, R′ = $-CH_2CH_2SCH_2CH_2-$ and $-(CH_2)_3S(CH_2)_3-$ supplied by Professor N. J. Leonard.

borates.—The procedure used is illustrated by methylphenyl-4′-chlorophenacylsulfonium tetrafluoroborate. Phenyl-4-chlorophenacyl sulfide (26.2 g, 0.1 mol) was added to trimethyloxonium tetrafluoroborate (14.8 g, 0.1 mol) in 200 ml of methylene chloride at room temperature. The mixture, after standing for 10 days, was diluted with ether and filtered. The methylphenyl-4-chlorophenacylsulfonium tetrafluoroborate was obtained as a white solid which after washing with ether and drying gave 34.2 g (94%), mp 155–157°. The salts prepared are listed in Table II.

Preparation of Dialkyl-4′-bromophenacylsulfonium Bromides.—The procedure used is illustrated with 4′-bromophenacyltetramethylenesulfonium bromide. Tetrahydrothiophene (17.6 g, 0.2 mol) and 2,4′-dibromoacetophenone (55.6 g, 0.2 mol) were mixed in 200 ml of benzene and heated to effect solution. After allowing the mixture to stand for 5 days the solid was removed by filtration. It was washed with benzene and dried in air to give 54.5 g (75%) of product, mp 123–125°. The sulfonium bromides prepared are listed in Table V.

Silver(I)-Catalyzed Oxidative Cleavage Reactions of Cyclic 1,2-Diols by Peroxydisulfate[1]

EARL S. HUYSER* AND LEROY G. ROSE

Department of Chemistry, University of Kansas, Lawrence, Kansas 66044

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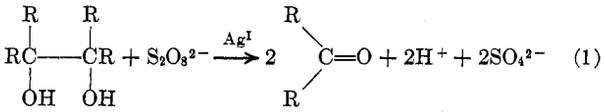
The oxidative cleavage rates of *cis*- and *trans*-1,2-cycloalkanediols by peroxydisulfate ($S_2O_8^{2-}$) in Ag^I-catalyzed reactions have been measured. The mechanistic implications of the observed reaction rates are discussed in terms of two mechanistic paths for the oxidative cleavage reactions. Path I proceeds by interaction of Ag^{III} with the diol. The kinetic data suggest the possible formation of a dsp^2 square planar complex as a reaction intermediate in oxidative cleavage by path I. The more rapid oxidative cleavage by path II is a free-radical chain reaction involving attack of the diol by Ag^{II} and apparently does not require formation of a cyclic complex between Ag^{II} and the diol.

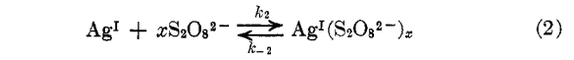
The oxidative cleavage reactions of glycols by peroxydisulfate in silver(I)-catalyzed reactions reported by Greenspan and Woodburn[2] have been the object of several mechanistic investigations.[3-8] Recently we



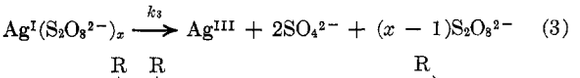
(1)

reported, on the basis of the kinetics of the reactions, that these oxidative cleavages were accomplished by two paths.[9] One route (path I) involves Ag^{III}, formed by oxidation of an $Ag^I(S_2O_8^{2-})_x$ complex, as the cleaving agent. The other route (path II) is a chain sequence of free-radical reactions involving Ag^{II} as the oxidative cleaving agent. Initiation of the chain sequence 6–8 is accomplished by reaction of Ag^{III} with Ag^I (reaction 5) yielding the chain-carrying Ag^{II} radical. Formation of Ag^{III} is the rate-determining factor for reaction by path I, whereas the rate of oxidative cleavage by path II, which is generally more rapid than reaction by path I, may depend on a variety of factors. Most significant of these is the partitioning of the Ag^{III} formed in reaction 3 between the substrate, resulting in cleavage by path I, and Ag^I which initiates the more rapid oxidation *via* the chain sequence. The relative amounts of cleavage by paths I and II depend on both the concentration of the substrate and its ability to interact with Ag^{III}. Thus, at lower substrate concentrations the overall rates of oxidative cleavage are faster, since more of the reaction is occurring by the more rapid free-radical chain sequence. On the other hand, if the substrate is capable of reacting readily with Ag^{III}, cleavage by the slower path I will be more prevalent than with substrates that react less readily with Ag^{III}. The latter situation allows for more extensive reaction of Ag^{III} with Ag^I, thereby initiating the faster oxidative cleavage by the free-radical chain reaction.

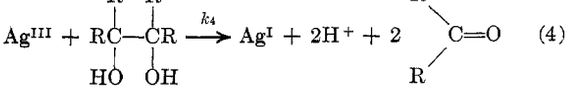
Path I



(2)



(3)



(4)

(1) This work was supported by a grant (AM-08517) from the U. S. Public Health Service.

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