From Diacetone Alcohol.—To finely powdered urea (12.0 g, 0.2 mole) suspended in 29.0 g (0.25 mole) of diacetone alcohol was added 15.0 g of sulfuric acid at such a rate that the temperature did not rise above 40°. The resultant mixture was stirred for 12 hr at a temperature of 40°, diluted with 50 ml of water, and then neutralized with 15% sodium hydroxide solution. The crystalline precipitate was filtered, washed with cold water, and recrystallized from methanol giving 18.5 g (66%) of product, mp 284–286° dec. The infrared spectrum was identical with that of the compound prepared above.

Anal. Found: C, 59.9; H, 8.7; N, 20.4.

2-Oxo-4,4,6-trimethylhexahydropyrimidine (IV). Hydrogenation of III.—A suspension of 140 mg of platinum oxide in 1.40 g (10 mmole) of III and 30 ml of acetic acid was hydrogenated at atmospheric pressure for 2 hr to give a hydrogen uptake equivalent to 9.6 mmoles. After removal of the catalyst and acetic acid, the remaining residue was neutralized with 10% sodium hydroxide solution yielding 1.28 g of crude solid product. It was recrystallized from ethanol–ether to give 1.08 g (76%) of IV: mp 256–258°; $\nu_{\max}^{\mathrm{KBr}}$ 3250, 3110, 2920, 1660, 1490, 1460, 1366, 1339, 1260, 1238, 1198, 1143, 760, 690, and 630 cm^{-1}.

Anal. Calcd for $C_7H_{14}N_2O$: C, 59.1; H, 9.9; N, 19.7. Found: C, 59.3; H, 9.5; N, 20.1.

2,7-Dioxo-4,5-dimethyldecahydropyrimido[4,5-*d*]pyrimidine (V).[6]—The method described by Zigeuner was utilized in the preparation of this compound: mp 279–280° dec; nmr spectrum broad at τ 2.50 (>NH), singlet at 4.61 (8a proton), multiplet at 6.00 (4 and 5 protons), multiplet at 7.60 (4a proton), and quartet at 8.40 (4- and 5-methyl protons); the area ratios of these peaks were 4:1:2:1:6.

Acknowledgment.—The authors wish to express their appreciation to Professor Walter J. Horton, University of Utah, for helpful suggestions and continued interest.

Displacement Reactions. XI. The Oxibase Parameters of Thio Anions[1]

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Thio anions, RS^-, are some of the best nucleophiles for S_N2 displacement reactions;[3-5] yet it is remarkable that accurate kinetic parameters are not available for many thio anions. It is the purpose of this note to communicate the oxibase scale[6] parameters[7] of numerous thio anions in water at 25° with numerous substrates. The parameters are also related to the basic properties of the ions.

The rate constants have been determined by measuring the change in the ultraviolet spectrum of the reaction mixture. Dilute deoxygenated solutions (10^{-4}–10^{-2} *M*) of the reactants in dilute buffer solutions (0.1 *M* maximum) were allowed to react in sealed quartz ultraviolet cells in a thermostated compartment. In some cases a stopper flow mixer was used if the half-times were <60 sec but >5 μsec.

The data at 25° in water are presented in Table I. The data represent about 400 kinetic experiments (temperatures 0–35°). The products of each reaction were analyzed.

TABLE I

KINETIC RATE CONSTANTS AT INFINITE DILUTION IN WATER AT 25.00°[a]

Anion[b]	Substrate[c]	pH range[d]	k_2 M^{-1} sec^{-1}[e]
$Et_2NCS_2^-$	β-Propiolactone[f]	6.7–7.5	0.304 ± 0.009
	Iodoacetate	5.9–8.2	2.20×10^{-2}
	Bromoacetate	5.9–8.2	5.38×10^{-3}
$EtSCS_2^-$	β-Propiolactone[f]	7.0–7.6	$6.70 \pm 0.04 \times 10^{-2}$
$EtOCS_2^-$	β-Propiolactone[f]	7.0–9.2	0.112 ± 0.003
	Iodoacetate	5.0–6.9	$1.66 \pm 0.05 \times 10^{-2}$
$CH_3CS_2^-$	β-Propiolactone[f,g]	7.3–11.9	$4.53 \pm 0.10 \times 10^{-2}$
CS_3^{2-}	β-Propiolactone[f]	9.2–11.9	0.42 ± 0.03

[a] The α and β values for each substrate and all kinetic measurements with the standard deviations are reported in ref 6, 7, and 13. [b] Anions as the sodium salts. Concentrations varied from 1.1 to 11.9 × 10^{-4} *M*. [c] Substrates as sodium salts. Concentrations varied from 1.7 to 15.1 × 10^{-3} *M* for the acetates and from 10^{-2} to 2 × 10^{-1} *M* for β-propiolactone. [d] pH range of the dilute buffer solutions. The rates were independent of the pH. [e] Second-order rate constant with the σ. [f] Kinetic rates were obtained only ionic strengths of μ = 0.01–0.10. Since the k_2 values are nearly independent of μ; no extrapolation μ = 0 was made. [g] An *E* value of 2.1 can be computed using the α and β value of musturd and the rate data of Ogston [A. G. Ogston, E. R. Holiday, J. St. L. Philpot, and L. A. Stocken, *Trans. Faraday Soc.*, **44,** 45 (1948)].

Using the oxibase scale[6,7]

$$\frac{\log k/k_0}{E} = \alpha + \beta\left(\frac{H}{E}\right)$$

where

$$X^- + AY \xrightarrow{k} AX + Y^-$$

$$H_2O + AY \xrightarrow{k_0} AOH + Y^- + H^+$$

and

$$2X^- = X_2 + 2e^-,\ E = \epsilon^0_{X^-} + 2.60\ \mathrm{v}$$
$$H^+ + X^- = HX,\ H = \mathrm{p}K_{\mathrm{a}X^-} + 1.74$$

and the α and β values for each substrate,[6,7] the *E* values were computed by a multiple regression technique[8] since the pK_a values are available in the literature[7] to compute *H* ($\equiv$pK_a + 1.74).[6] The oxibase scale values are listed in Table II and compared with the values of other thio anions.

The thio anions are excellent nucleophiles on carbon because they are very easily oxidized.

Calculations have been made of the properties of the ions using an Extended[9] Huckel Method[10] but using all the 1s–3p electrons in an SCF program.[10] However, even the simple π-LCAO-MO-SCF method on the

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[1] Paper X: R. E. Davis, R. Nehring, S. Molnar, and L. A. Suba, *Tetrahedron Letters*, in press.

[2] Alfred P. Sloan Fellow, 1962–1966.

[3] C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

[4] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[5] E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press Co., New York, N. Y., 1964.

[6] J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954); **78**, 1819 (1956). J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

[7] R. E. Davis, "Survey of Progress in Chemistry," Vol. 2, A. Scott, Ed., Academic Press Inc., New York, N. Y., 1964, pp 189–238.

[8] Wald Method with Confidence Bands. Program in Fortran IV is available upon request. We assume errors in all variables: *k*, *k*₀, *α*, *β*, *E*, and *H*.

[9] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[10] The EHM-SCF program is similar to that reported by E. B. Moore, Jr., *Inorg. Chem.*, **4**, 1084 (1965).

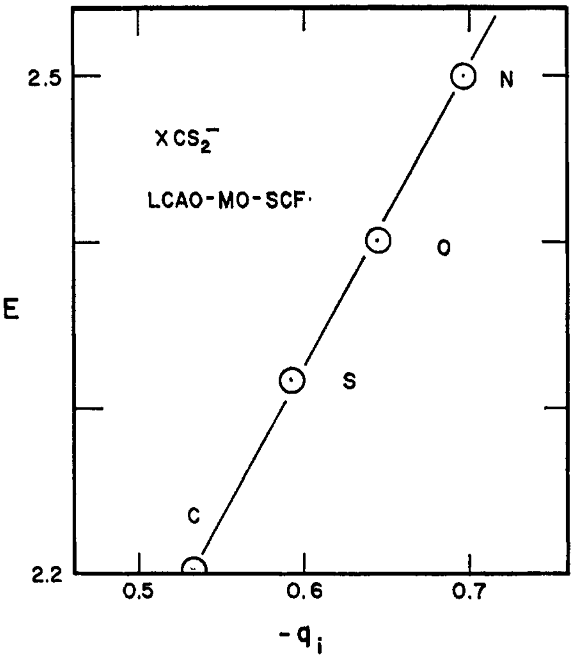

Figure 1.—Plot of kinetic E values in volts *vs.* the charge density, q_i, on the sulfur atom in dithioacetate, ethyl trithiocarbonate, ethyl xanthate, and diethyl dithiocarbamate. E is the oxidative dimerization potential plus 2.60 v for $2RS^- \rightleftharpoons RSSR + 2e^-$ in water at 25°.

Table II

Oxibase Scale Parameters of Thio Anions in Water at 25°

Nucleophile	E, v[a]	H	H/E
$H_2NCH_2CH_2S^-$ [b]	3.08	12.5	4.06
S^{2-} [c]	3.08	14.6	4.74
$H_3\overset{+}{N}CH_2CH_2S^-$ [b]	2.88	10.3	3.58
HS^- [c]	2.60	8.70	3.35
SO_3^{2-} [c]	2.57	9.00	3.50
O_3SS^{2-} [c]	2.52	3.6	1.43
$Et_2NCS_2^-$ [a]	2.49	5.74	2.29
CS_3^{2-} [a]	2.45	10.47	4.27
$EtOCS_2^-$ [a]	2.40	3.44	1.43
$EtSCS_2^-$ [a]	2.32	3.29	1.42
$CH_3CS_2^-$ [a]	2.18	4.29	1.97
NCS^- [c]	1.83	(1)	0.55

[a] This study. All are experimental values. Average σ ±0.03 v. [b] See ref 1. [c] Values reported by J. O. Edwards [ref 6, p 1540].

XCS_2^- ions (X = C, S, O, N) yields interesting results.[11] In particular the amount of charge density on the thio atom (as measured by $-q_i$) is related to the oxibase constant, E. The data are presented in Figure 1.

The basic ideas behind the oxibase scale[6,7] are simple and easy to use. Realistic model systems[12] are used to construct the linear free energy equations.[13]

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(11) M. J. Janssen, *Rec. Trav. Chim.*, **79**, 1066 (1960).

(12) J. E. Leffer and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 128–146, 251–254.

(13) R. E. Davis, *J. Am. Chem. Soc.*, **87**, 3010 (1965). The substrate parameters (α and β) for these materials used in obtaining the kinetic E values reported in Table II are reported in this reference. An estimate of all σ values, the standard deviations, of α and β are also given.

A Facile Route to Ferrocenyl- and 2-Thienylarylacetylenes[1a]

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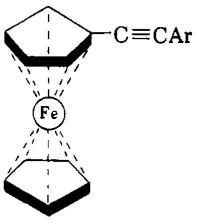
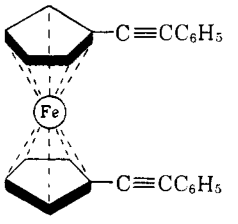
Stephens and Castro have recently described a useful new synthesis for tolane (diphenylacetylene) and substituted tolanes utilizing aryl iodides and cuprous phenylacetylide in refluxing pyridine.[2] It was of interest to us to determine if this procedure could be employed for the formation of ferrocenyl and certain heterocyclic arylacetylenes, and to study the chemistry of these substances. Our preliminary studies have been successful, and are reported herein.

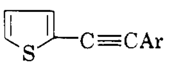
In a typical reaction, approximately equimolar amounts of iodoferrocene and cuprous phenylacetylide were refluxed in pyridine for 8 hr under nitrogen. Subsequent work-up afforded an 84% yield of ferrocenylphenylacetylene (**1a**).[3] In an analogous manner,



1a, Ar = C_6H_5
b, Ar = $FeC_{10}H_9$



2



3a, Ar = C_6H_5
b, Ar = $FeC_{10}H_9$

the reaction between iodoferrocene and cuprous ferrocenylacetylide produced diferrocenylacetylene (**1b**) in 85% yield. Further, while the studies of Stephens and Castro were limited to monoiodobenzene derivatives, we have found that treatment of 1,1′-diiodoferrocene with an excess of cuprous phenylacetylide under similar conditions produces the diacetylene 1,1′-bis(phenylethynyl)ferrocene (**2**) in approximately 60% yield.

The iodoferrocenes used in these reactions are obtained in reasonably good yields from the readily available chloromercuriferrocenes,[4–7] or from the reaction of lithioferrocenes with iodine at low temperatures.[8] Ferrocenylacetylene has very recently become readily available by means of the reaction of acetylferrocene with the Vilsmeier complex from dimethyl-

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(1) (a) Part XI of a series "Organometallic π-Complexes." Part X: V. Mark and M. D. Rausch, *Inorg. Chem.*, **3**, 1067 (1964). Part IX: M. D. Rausch, *J. Org. Chem.*, **29**, 1257 (1964). Part VIII: M. D. Rausch and V. Mark, *ibid.*, **28**, 3225 (1963). (b) National Science Foundation Undergraduate Research Fellow, 1964.

(2) R. D. Stephens and C. E. Castro, *J. Org. Chem.*, **28**, 3313 (1963).

(3) The preparation of **1a** in 48% yield using a similar reaction between bromoferrocene and cuprous phenylacetylide in dimethylformamide has recently been briefly described [A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Dokl. Akad. Nauk SSSR*, **154**, 158 (1964)].

(4) A. N. Nesmeyanov, E. G. Perevalova, and O. A. Nesmeyanova, *ibid.*, **100**, 1099 (1955).

(5) M. D. Rausch, *J. Org. Chem.*, **28**, 3337 (1963).

(6) M. Rosenblum and R. W. Fish, *ibid.*, **30**, 1253 (1965).

(7) M. D. Rausch, R. F. Kovar, A. Siegel, T. H. Mladineo, and L. P. Klemann, "Organometallic Syntheses," Academic Press Inc., New York, N. Y. in press.

(8) M. D. Rausch and R. F. Kovar, to be published.