

diethoxythietane 1,1-dioxide which after heating at reflux for 2 hr. gave a homogeneous solution. Acidification with 10% hydrochloric acid precipitated 1.60 g. (58%) of benzylsulfonylacetic acid, which after recrystallization from water and ethanol melted at 136–138°. A mixture melting point with an authentic sample²⁰ showed no depression (m.p. 136–138°) and their infrared spectra were superimposable.

If the basic hydrolysis is carried out with sodium hydroxide in ethanol the sodium salt of the acid precipitates (52%) from the solution and on recrystallization from ethanol and water melts at 210–211°.

Anal. Calcd. for C₉H₉NaSO₄: C, 45.76; H, 3.84; Na, 9.74; S, 13.58. Found: C, 45.40; H, 3.74; Na, 9.75; S, 13.50.

2-Phenyl-3-ethoxythiete 1,1-Dioxide.—2-Phenyl-3,3-diethoxythietane 1,1-dioxide (9.00 g., 0.03 mole) was dissolved in a solution of sodium ethoxide prepared from 0.69 g. (0.03 g.-atom) of sodium in 150 ml. of absolute ethanol under a nitrogen atmosphere. The solution was heated at 70° for 5 hr. after which time the solution had taken on a yellow color, but no formation of a precipitate was observed as with sodium hydroxide in ethanol. The solution was cooled and 150 ml. of water was added forming a yellow precipitate. Acidification with dilute sulfuric acid removed most of the yellow color. The solid was recrystallized from absolute ethanol, giving 2.71 g. (m.p. 128–132°) of product. An analytical sample was prepared by suspending 1.0 g. of the solid in boiling *n*-hexane (30 ml.) and adding ethanol dropwise until dissolution was complete. Cooling slowly gave long white needles, m.p. 132–134°.

Anal. Calcd. for C₁₁H₁₂SO₃: C, 58.93; H, 5.40; S, 14.31; mol. wt., 224. Found: C, 59.00; H, 5.32; S, 14.29; mol. wt., 228 (CHCl₃).

Pyrolysis of 3,3-Diethoxythietane 1,1-Dioxide.—Over a period of 25 min., 10.0 g. of the adduct was dropped through a pyrolysis tube packed with 4-mm. glass beads and externally heated at 500° under a slow nitrogen flow. Excessive decomposition occurred and tar formed throughout the tube. However, 2.0 g. of a black oil with a very acrid odor was collected in an ice-cooled container, and distilled over a large range (80–115°) to a colorless acidic liquid. Vapor phase chromatographic analysis

indicated the presence of about 76% ethanol and 20% acetic acid with several other peaks. The Dry Ice trap was found to contain 2.0 g. of a yellow liquid which was mostly sulfur dioxide.

Pyrolysis of 2-Phenyl-3,3-diethoxythietane 1,1-Dioxide.—Pyrolysis was achieved by distilling 5.5 g. (0.02 mole) of the adduct at a 200° pot temp. through a 6-in. Vigreux column at 12 mm. pressure. A yellow liquid, 0.67 g., distilled between 130–140° (12 mm.). A portion of this oil when boiled in a 10% sodium hydroxide solution yielded cinnamic acid on acidification. The infrared spectrum of the oil was identical with that of a known sample of ethyl cinnamate. Vapor phase chromatographic analysis indicated 85% purity and the retention times of the above oil and ethyl cinnamate were identical.

Lithium Aluminum Hydride Reduction of 2-Phenyl-3,3-diethoxythietane 1,1-Dioxide.—Finely ground lithium aluminum hydride (7.6 g., 0.20 mole) was suspended in 150 ml. of anhydrous ether. A solution of 5.40 g. (0.02 mole) of 2-phenyl-3,3-diethoxythietane 1,1-dioxide, dissolved in 50 ml. of anhydrous tetrahydrofuran, was added dropwise to the hydride mixture over a period of 30 min. After stirring at 25° for 6 hr. the gray mixture was cautiously poured over 300 ml. of ice-water. The hydrolysate was then made strongly acidic with 200 ml. of 6 *N* hydrochloric acid. The solution was steam distilled until 400 ml. of distillate had been collected, the aqueous layer was extracted with ether, and the combined extracts were dried over Na₂SO₄. The ether was then removed by distillation at 35–37° and the yellow residue which remained was distilled at 73° (4.5 mm.), giving 0.50 g. (17%) of phenylacetone. The infrared spectrum showed a strong carbonyl absorbance at 5.8 μ.

Anal. Calcd. for C₉H₁₀O: C, 80.56; H, 7.51; mol. wt., 134. Found: C, 80.34; H, 7.79; mol. wt., 139 (CHCl₃).

A yellow 2,4-dinitrophenylhydrazone was obtained; m.p. 150–151° from 95% ethanol (lit.²¹ m.p. 153°).

Acknowledgment.—The authors gratefully acknowledge the support of this work by the Gulf Research and Development Corporation and by the National Institutes of Health under grant No. CY-4536.

(21) C. D. Hodgman, Ed., "Tables for Identification of Organic Compounds," Chemical Rubber Publishing Co., Cleveland, O., 1960, p. 95.

(20) G. G. Stoner, *J. Am. Chem. Soc.*, **63**, 1481 (1941)

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA 13, GA.]

Polar Effects on Rates and Equilibria. VIII. Double Bond-No Bond Resonance¹

BY JACK HINE

RECEIVED JANUARY 15, 1963

Thermochemical data on the polyfluorides of methane show that these compounds are stabilized (relative to the stability that would be expected from carbon-hydrogen bonds like those in methane and a carbon-fluorine bond like that in methyl fluoride) by about 3.2 kcal./mole for each double bond-no bond resonance structure

(*e.g.*, $\overset{\oplus}{\text{F}}=\overset{\ominus}{\text{C}}\text{F}_2$) that may be written. Much less stabilization of this type would be expected for the chlorides and bromides of methane and much less (if any) is found. It is pointed out that the data may be explained by a strong attraction between geminate fluorine atoms or by the relative exemption of pairs of fluorine atoms from a strong repulsion operating between most pairs of geminate atoms. However, from the ordinary methods of estimating the magnitudes of London forces, van der Waals repulsions, and polar interactions between substituents, it appears that these factors do not explain the data at hand. From the heats of formation of trioxane, 1,3-dioxane, 1,4-dioxane, tetrahydropyran, and related compounds it appears that two oxygen atoms attached to the same saturated carbon atom give about as strong a double bond-no bond resonance interaction as two fluorine atoms do. Such resonance involving oxygen-oxygen interaction also explains the isomerization of glycol ethers to acetals and the following hydrolysis rate sequence: CH₃OEt < CH₂(OEt)₂ < CH(OEt)₃ > C(OEt)₄. There is also evidence for a number of examples of double bond-no bond resonance involving two different atoms attached to the same saturated carbon atom.

Introduction

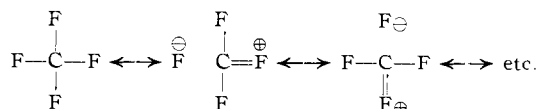
In 1937, Brockway reported that carbon-fluorine bond distances in the fluoromethanes and the fluorochloromethanes are significantly shorter in compounds with several fluorine atoms attached to the same carbon atom than in monofluorides.^{2,3a} The shortened bond distances were explained in terms of the following type

(1) Much of this material was presented at the 18th National Organic Symposium of the American Chemical Society, Columbus, Ohio, June 20, 1963. For paper VII in this series see J. Hine and H. E. Harris, *J. Am. Chem. Soc.*, **85**, 1476 (1963).

(2) L. O. Brockway, *J. Phys. Chem.*, **41**, 185, 747 (1937).

(3) L. Pauling, "The Nature of the Chemical Bond," 3rd. Ed., Cornell University Press, Ithaca, N. Y., 1960: (a) pp. 314–315; (b) p. 264; (c) p. 260.

of resonance



which will be referred to as *double bond-no bond resonance*.⁴ This resonance should stabilize the molecule

(4) The present paper shall discuss only double bond-no bond resonance in which an atom attached to carbon is no-bonded *with* the bonding electron pair. Hyperconjugation involving the no-bonding of hydrogen, one type of double bond-no bond resonance in which an atom is no-bonded *without* the bonding electron pair, has been discussed in detail by other investigators.

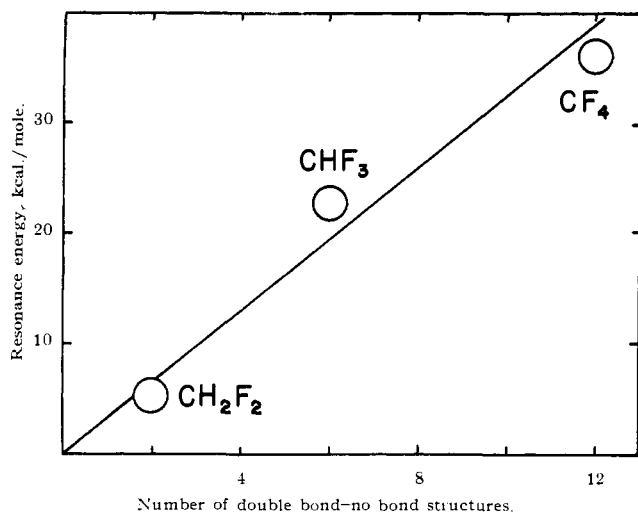


Fig. 1.—Plot of number of double bond–no bond structures vs. resonance energy of fluoromethanes.

(with respect to its dissociated atoms) and thus increase the strength of the bonds. Since stronger bonds (of a given kind) are usually shorter bonds, the suggested resonance explains the observed bond shortening and also many qualitative observations that had been made on the unreactivity of trifluoromethyl and difluoromethylene groups in organic molecules.⁵ Many subsequent observations on organic polyfluorides have been explained in terms of such resonance and others could have been.

The concept of double bond–no bond resonance has been criticized, sometimes as a part of a general criticism of the theory of resonance, and it has also been expressed alternatively in terms of molecular orbitals.⁶

In the present paper various types of evidence for double bond–no bond resonance, the plausibility of certain alternative interpretations of this evidence, and the effect of molecular structure on double bond–no bond resonance will be discussed. In addition, several types of evidence will be shown to point to stabilization by such resonance in types of compounds, such as those with several oxygen atoms attached to the same saturated carbon atom, for which it does not appear to have been suggested previously.

Discussion

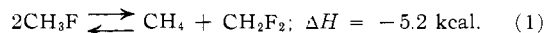
Double Bond–No Bond Resonance with Organic Polyfluorides.—The strongest evidence for double bond–no bond resonance in organic polyfluorides comes from quantitative determinations of heats of combustion, heats of reactions, and equilibrium constants for various reactions. Patrick has summarized much of the thermochemical data on organic fluorides.⁷ In Table I are listed the carbon–halogen bond energies he compiled, computed on the usual basis; that is, in each case the carbon–hydrogen bond energy is assigned a value equal to one-fourth the atomization energy of methane. In the case of the fluorochloromethanes the carbon–chlorine bond energy in each case is taken as 78.0 kcal., the value observed in methyl chloride. The carbon–fluorine bond energies are seen to increase steadily as more and more fluorine atoms become attached to the same carbon atom, so that methylene

fluoride, fluoroform, and carbon tetrafluoride are 5.2, 22.8, and 36 kcal./mole more stable, respectively, than would be expected on the basis of the carbon–fluorine bond energy in methyl fluoride (and the carbon–hydrogen bond energy in methane). In Fig. 1, a plot

TABLE I
BOND ENERGIES IN HALOMETHANES⁷

Halide	BE _{C-F}	Halide	BE _{C-X}
CH ₃ F	107	CH ₃ Cl	78.0
CH ₂ F ₂	109.6	CH ₂ Cl ₂	77.9
CHF ₃	114.6	CHCl ₃	78.3
CF ₄	116	CCl ₄	78.2
CCl ₃ F	109.3	CH ₃ Br	66.6
CCl ₂ F ₂	111.5	CH ₂ Br ₂	65.5
CClF ₃	115.5	CHBr ₃	65.1
		CBr ₄	66.6

of the number of double bond–no bond structures (2, 6, and 12, respectively) that can be written for the polyfluoromethanes vs. their resonance energies (extra stabilities as given in the previous sentence) is seen to give a reasonably straight line. From the slope of the line it may be concluded that a resonance energy of roughly 3.2 kcal. per double bond–no bond structure (or 6.5 kcal. per fluorine–fluorine interaction) may be expected. The extra resonance stabilization of methylene fluoride, for example, may be seen in the fact that the disproportionation of methyl fluoride to methane and methylene fluoride is exothermic by 5.2 kcal./mole, according to the data in Table I. According to



Benson and Buss's first-order approximation, from which deviations larger than 1.5 e.u. (corresponding to 0.45 kcal. in free energy at 27°) are rare, the entropy change for this reaction will be only that due to symmetry changes.⁸ Neglecting such symmetry changes, the free-energy change will be equal to the enthalpy change and therefore the equilibrium constant for the reaction will be almost 10⁴ at room temperature. This large a free-energy change for such a disproportionation reaction is unusual⁸; it is not found in the corresponding reactions of polychloro- or polybromomethanes and it suggests some stabilizing interaction that is particularly strong with polyfluorides.

Double bond–no bond resonance would be expected to be much more important for fluorine than for any of the other halogens. Because of fluorine's much greater electronegativity, structures involving a halogen no-bonded as an anion should contribute most when that halogen is fluorine. In view of the greater ease with which fluorine shares its unshared electron pairs (as shown, for example, by its much smaller Hammett *p*-substituent constant^{9a}), structures involving a double bond to halogen and a positive charge on the halogen should also contribute most when the halogen is fluorine.

The fact that the transformation of polyfluoroethylene derivatives to various saturated compounds is, in general, much more exothermic than the corresponding reactions of the analogous fluorine-free olefins^{7,10} can be rationalized by the hypothesis that double bond–no bond resonance is much more important when several fluorine atoms are attached to the same saturated carbon atom than when they are attached to an unsaturated carbon atom. It may alternatively be hypothesized that fluorine atoms attached to the unsaturated carbon atoms of olefins decrease the stability

(5) For some early examples of this unreactivity see F. Swarts, *Bull. sci. acad. roy. Belg.*, [5] **8**, 343 (1922); and A. L. Henne, in H. Gilman's, "Advanced Organic Chemistry," Vol. 1, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, Chapter 11.

(6) Cf. J. P. A. Williams, *Trans. Faraday Soc.*, **57**, 2089 (1961); *Tetrahedron*, **18**, 1477 (1962), and references cited therein.

(7) C. R. Patrick, "Advances in Fluorine Chemistry," Vol. 2, Butterworths, Washington, D. C., 1961, Chapter 1.

(8) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).

(9) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962: (a) p. 87; (b) pp. 116–119.

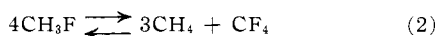
(10) C. R. Patrick, *Tetrahedron*, **4**, 26 (1958).

of the olefins whether more than one fluorine atom is attached to the same carbon atom or not. The present data on such compounds as vinyl fluoride, 1,2-difluoroethylene, etc., do not seem adequate to permit a decision between the two hypotheses.

Alternative Interpretations of the Evidence for Double Bond-No Bond Resonance.—There are other factors that must influence the stability of polyfluoromethane derivatives whether double bond-no bond resonance is of importance or not. Any assessment of the significance of double bond-no bond resonance must include an estimate of whether the relevant data may be explained, wholly or in part, in terms of these other factors.

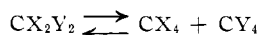
On the basis of electrostatic principles, reaction 1 may be thought of as bringing the two dipoles consisting of carbon-fluorine bonds together in such a way as to cause their positive ends to lie on top of one another. This should be energetically unfavorable and should therefore cause reaction 1 to be endothermic.

The particular stability of polyfluoromethane derivatives could be explained in terms of a particularly strong attraction between fluorine atoms, or by pairs of fluorine atoms being relatively exempt from a type of strong repulsion found between most pairs of atoms. London forces probably represent the most important attractive forces (other than bonding) that operate between atoms that are relatively close to each other. In certain disproportionations, London forces (dispersion energy or electron-correlation energy) become important. Thus in the analog of reaction 1 in which F is methyl, the enthalpy of reaction may be calculated¹¹ to be -2.24 kcal./mole. Pitzer and Catalano described calculations of the dispersion energies of the lower saturated aliphatic hydrocarbons that largely explain the heats of reaction in disproportionations of ethane to give propane, isobutane, neopentane, etc. The application of their method of calculation^{12,13} to the disproportionation of methyl fluoride to methane and carbon tetrafluoride



gives a change in dispersion energy of about -4 kcal./mole (calculated using $109^\circ 28'$ bond angles, 1.10 Å carbon-hydrogen bond lengths, and carbon-fluorine bond lengths of 1.39 and 1.337 Å in methyl fluoride and carbon tetrafluoride, respectively^{14a}), far less than the actual enthalpy of reaction, -36 kcal./mole. Thus, unless this method of calculating the dispersion energy is highly inaccurate, the enthalpy change for reaction 2 is much too large to be rationalized in terms of London forces. Petersen and Pitzer have already estimated that not more than half of the enthalpy of certain disproportionations of polychlorofluoromethanes can be attributed to changes in dispersion energy.¹³

The simple qualitative theory of steric hindrance usually employed by organic chemists also provides no reasonable explanation for the great relative stability of compounds with more than one fluorine atom attached to the same carbon atom. In fact, in general, in such equilibria as



steric repulsions should tend to force the equilibrium to the left to avoid crowding all the larger atoms around the same carbon atom.

(11) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

(12) K. S. Pitzer and E. Catalano, *J. Am. Chem. Soc.*, **78**, 4844 (1956).

(13) D. E. Petersen and K. S. Pitzer, *J. Phys. Chem.*, **61**, 1252 (1957).

(14) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955: (a) pp. 697-702; (b) pp. 88-89.

Consider, in a more quantitative fashion, reaction 2, which may be depicted as involving the transformation of twelve hydrogen-fluorine interactions into six hydrogen-hydrogen interactions and six fluorine-fluorine interactions. Although Pauling stated that "a univalent atom can be considered as a sphere that is whittled down on the side of the bond,"^{3b} if we assume very much whittling in the present argument, steric repulsions will be too small to explain our data. If the van der Waals radii of the various atoms are to be the same in all directions,¹⁵ the distance between two hydrogen atoms in methane (or, we assume, in methyl fluoride) is 0.60 Å. less, the distance between two fluorine atoms in carbon tetrafluoride is 0.52 Å. less, and the distance between the fluorine atom and a hydrogen atom in methyl fluoride is 0.51 Å. less than the sum of the van der Waals radii^{3c} of the two atoms. Since the crowding between a hydrogen and a fluorine atom is thus no more than that between two hydrogen atoms or two fluorine atoms, when measured in terms of distance, it seems unlikely that it would be significantly greater when measured in terms of energy. To explain the enthalpy of reaction 2 the energy of repulsion between a hydrogen and a fluorine atom in methyl fluoride would have to exceed the mean of the repulsion energy of two hydrogen atoms in methane and that of two fluorine atoms in carbon tetrafluoride by 3 kcal./mole. Since repulsion energies do not usually reach 3 kcal./mole until the crowding between two atoms approaches 1.0 Å.,¹⁶ it seems extremely unlikely that differences of 3 kcal./mole would result from 0.5 - 0.6 Å. crowdings.

With sufficiently large van der Waals radii and with van der Waals potential functions that yield more repulsion energy for a given amount of crowding between hydrogen and fluorine than between two hydrogen atoms or two fluorine atoms, it would be possible to rationalize the highly exothermic character of reaction 2. In view of our present ignorance of van der Waals potentials, however, the enthalpy of reaction 2 seems more easily explained by double bond-no bond resonance than by van der Waals forces.

Double Bond-No Bond Resonance Involving Oxygen-Oxygen Interactions.—Although double bond-no bond resonance would be expected to become less important and apparently does become less important as we move down the periodic table from fluorine to the other halogens, it is not clear what would be expected as we move to the left in the periodic table from fluorine to oxygen and nitrogen. Oxygen and nitrogen are less electronegative than fluorine but they are far better at sharing their unshared electron pairs. Thus since one of the factors of importance decreases while the other one increases, we cannot, without a more quantitative treatment, predict whether the interaction of two alkoxy groups or of two amino groups attached to the same saturated carbon atom should be larger or smaller than that of two fluorine atoms.

There have been data in the literature for a long time that point to considerable double bond-no bond resonance in such compounds as acetals, which have two oxygen atoms attached to the same carbon atom. Stabilization due to such resonance can be inferred

(15) For arguments that van der Waals repulsions between two atoms attached to the same atom are important, see L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

(16) This follows from calculations using a van der Waals potential function for neon and from the generalization that the shape of van der Waals potential curves is relatively independent of the nature of the atoms involved.¹⁷

(17) F. H. Westheimer, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., pp. 530, 531, 548.

from the determination of heats of combustion made by Thomsen and others around the turn of the century. In Klages' correlation of heats of combustion a stabilizing factor of 11.8 kcal./mole is added for a compound containing an acetal linkage.¹⁸ In Wheland's treatment of Klages' work this factor is changed to 3.0 kcal./mole.^{14b} The value of the factor is quite dependent on the manner in which the remainder of the correlation is made.

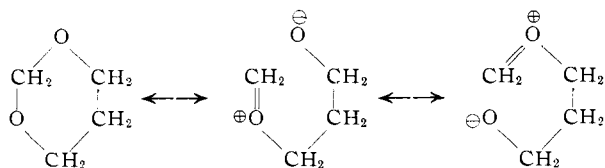
To illustrate the type of thermochemical data that point to oxygen-oxygen double bond-no bond resonance, the heats of formation of several cyclic ethers and the analogous hydrocarbons are listed in Table II.

TABLE II
HEATS OF FORMATION IN THE GAS PHASE AT 25° (IN KCAL./MOLE)

Compound	$-\Delta H_f^\circ$	$\Delta(\Delta H_f^\circ)^a$	Ref.
Cyclohexane	29.5		11
Tetrahydropyran	52.6	23.1	19
1,4-Dioxane	76.0	23.4	19
1,3-Dioxane	81.5	28.9	19
	83.6	31.0	20
1,3,5-Trioxane	120.8	39.3 (37.2)	19
Cyclopentane	18.5		11
Tetrahydrofuran	43.5	25.0	21
1,3-Dioxolane ^b	71.7	28.2	21
	72.9	29.4	21

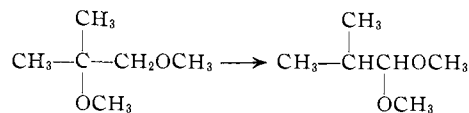
^a Difference between the heat of formation of this compound and the one in which one of its oxygen atoms has been replaced by a methylene group. ^b These data are calculated on the basis of the assumption that the heat of vaporization of 1,3-dioxolane is the same as that of tetrahydrofuran.

Snelson and Skinner pointed out, in the case of the compounds with six-membered rings, that the presence of two oxygen atoms attached to the same carbon atom leads to considerably increased stability,¹⁹ but they suggested no explanation for this increased stability. These data involving six-membered rings may be rather closely approximated, particularly if the data on 1,3-dioxane due to Skuratov and co-workers²⁰ is accepted, by the generalization that each replacement of a methylene group by an oxygen atom increases $-\Delta H_f^\circ$ by 23.3 kcal., and the presence of two oxygen atoms on the same carbon atom produces an additional increase of 7.0 kcal. The data on five-membered ring compounds²¹ show a somewhat similar relationship. With modifications to allow for the fact that carbon-oxygen bond strengths depend on whether the carbon atom is methyl, primary, secondary, or tertiary, this generalization can be applied to other acetals. A contribution of 7.0 kcal. per oxygen-oxygen interaction corresponds to 3.5 kcal. per double bond-no bond structure and is not significantly different from the contribution of 6.5 kcal. per fluorine-fluorine interaction already estimated.



Further evidence for double bond-no bond resonance involving oxygen-oxygen interactions may be found in the course, relative rate, or position of equilibrium of various organic reactions. Ley and Vernon, for example, found that in the presence of an acid catalyst

in methanol solution, 1,2-dimethoxy-2-methylpropane rearranges largely, at least, to 1,1-dimethoxy-2-methylpropane.²² The preferential migration of the methoxy



group from the tertiary carbon atom to a primary carbon atom occurs in spite of the fact that oxygen atoms usually show a preference for attachment to tertiary carbon, as shown, for example, by the fact that the gas-phase heat of formation of *t*-butyl alcohol at 25° (-74.9 kcal.) is 7.0 kcal. more negative than that of isobutyl alcohol.²³

The effect of the successive introduction of α -ethoxy substituents on the rate of acid-catalyzed hydrolysis of methyl ethyl ether is also striking. Second-order rate constants for the hydrolysis of compounds of interest in aqueous solution at 25° are listed in Table III.²⁴⁻²⁶

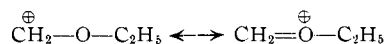
TABLE III
RATE CONSTANTS FOR ACID-CATALYZED HYDROLYSIS OF CERTAIN ETHOXY COMPOUNDS IN WATER AT 25°²⁴⁻²⁶

Compound	k , l. mole ⁻¹ sec. ⁻¹
CH ₃ OC ₂ H ₅ (SN1) ^a	~10 ^{-19a}
C ₂ H ₅ OC ₂ H ₅	2.4 × 10 ⁻¹³
CH ₂ (OC ₂ H ₅) ₂	1.8 × 10 ⁻³
CH(OC ₂ H ₅) ₃	5.4 × 10 ²
C(OC ₂ H ₅) ₄	9.0 × 10 ¹
CH ₃ CH(OC ₂ H ₅) ₂	7.3 × 10 ⁻¹
CH ₃ C(OC ₂ H ₅) ₃	2.1 × 10 ⁴
C ₂ H ₅ C(OC ₂ H ₅) ₃	1.3 × 10 ⁴

^a Estimate of the rate constant for formation of the methyl cation.²⁷

The rate of acid-catalyzed hydrolysis of methyl ethyl ether appears not to have been studied, but it is probably within a couple of powers of ten of that of diethyl ether, for which a rate constant is listed. Since all the acetals and orthoesters in the series almost undoubtedly hydrolyze by the SN1 mechanism, it is more relevant to compare their rate constants with the rate constant for the SN1 cleavage of methyl ethyl ether at the methyl-oxygen bond. No such rate constant has been determined, of course, but an estimate of its value is included in the table.²⁷

The tremendous increase in reactivity brought about by the introduction of the first α -ethoxy substituent into methyl ether can be explained (qualitatively) in terms of resonance stabilization of the intermediate carbonium ion, and hence of the transition state leading to that carbonium ion. The increase in reactivity pro-



duced by the introduction of a second α -ethoxy substituent (to give ethyl orthoformate) is much smaller. This decrease in the magnitude of the α -ethoxy substituent effect seems qualitatively understandable since as the stability of the carbonium ion increases, the transition state will occur earlier in the reaction and

(22) J. B. Ley and C. A. Vernon, *J. Chem. Soc.*, 2987 (1957).

(23) H. A. Skinner and A. Snelson, *Trans. Faraday Soc.*, **56**, 1776 (1960).

(24) A. Skrabal and A. Zahorka, *Monatsh.*, **63**, 1 (1933).

(25) P. M. Leininger and M. Kilpatrick, *J. Am. Chem. Soc.*, **61**, 2510 (1959).

(26) J. N. Brønsted and W. P. K. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

(27) This estimate is based on the assumption that the acid-catalyzed cleavage of ethyl isopropyl ether involves the formation of an isopropyl cation. Since α -methyl substituents usually increase SN1 reactivity by about 10²- or 10⁴-fold, and since the rate constant for the acid hydrolysis of ethyl isopropyl ether is 2.5 × 10⁻¹² l. mole⁻¹ sec.⁻¹ at 25°, the estimate of the SN1 rate for methyl ethyl ether is 10⁻¹⁹ l. mole⁻¹ sec.⁻¹.

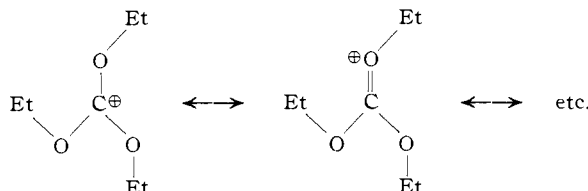
(18) F. Klages, *Chem. Ber.*, **82**, 358 (1949).

(19) A. Snelson and H. A. Skinner, *Trans. Faraday Soc.*, **57**, 2125 (1961).

(20) S. M. Skuratov, A. A. Strepikheev, S. M. Shtekher, and A. V. Volokhina, *Doklady Akad. Nauk S.S.S.R.*, **117**, 263 (1957).

(21) J. H. S. Green, *Quart. Rev. (London)*, **15**, 125 (1961).

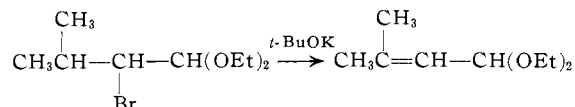
therefore substituent effects will be smaller.^{9b} When another α -ethoxy substituent is introduced (to give ethyl orthocarbonate) its effect is not just reduced, it is reversed. The decreased reactivity of ethyl orthocarbonate relative to ethyl orthoformate does not seem explicable on the basis of argument concerning the location of the transition state along the reaction coordinate. A plausible explanation may be made, however, in terms of resonance stabilization of the reactant. If ethyl orthocarbonate is stabilized by 3.5 kcal. for each of the twelve double bond-no bond structures that may be written, its total resonance energy is 42 kcal. (and that of ethyl orthoformate is 21 kcal.). In the intermediate carbonium ion such double bond-no



bond resonance would be far less important (it would involve placing like charges near each other, for example), and even in the transition state there would be a large decrease in the double bond-no bond resonance stabilization.

Certain alternative explanations of the relative unreactivity of ethyl orthocarbonate seem less plausible. Since the influence of the last α -ethoxy substituent differs from that of the previous one by a factor of 1.8×10^6 , the effect to be explained is a large one. Steric hindrance to protonation seems an improbable explanation since ethyl orthopropionate, which is highly reactive, must be equally hindered or more so. It is possible that resonance stabilization of the intermediate carbonium ion $(\text{EtO})_3\text{C}^+$ is somewhat decreased by the difficulty in getting the central carbon atom, the three oxygen atoms, and the three α -carbon atoms of the ethyl groups in the same plane. From examination of molecular models, however, only certain conformations of such a coplanar species seem strained, so that only a relatively small effect (largely in the entropy term) would be expected. Furthermore, in the transition state, which should come fairly early in the reaction in this case, the coplanar form has not yet been reached and any strain should be smaller.

With *gem*-dialkoxy compounds as with *gem*-difluorides there is some evidence that double bond-no bond resonance is much more important when the interacting groups are attached to saturated carbon than when they are attached to unsaturated carbon. McElvain, Clarke, and Jones, for example, found that the dehydrohalogenation of the diethylacetal of α -bromoiso-valeraldehyde gives the acetal of an α,β -unsaturated aldehyde rather than the ketene acetal (which was shown to be stable under the reaction conditions).²⁸



This occurs in spite of the fact that when only one alkoxy group is present vinyl ethers are formed.²⁹ Thus, although one alkoxy group on a double bond stabilizes a compound³⁰ (relative to the corresponding saturated compound), it is possible that two *gem*-alkoxy groups do not.

(28) S. M. McElvain, R. L. Clarke, and G. D. Jones, *J. Am. Chem. Soc.*, **64**, 1966 (1942).

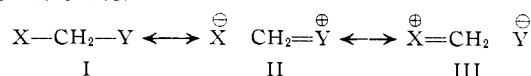
(29) Cf. W. M. Lauer and M. A. Spielman, *ibid.*, **53**, 1533 (1931).

(30) Cf. R. Paul, M. Fluchaire, and G. Collardeau, *Bull. soc. chim. France*, 668 (1950).

Other Types of Double Bond-No Bond Resonance.—

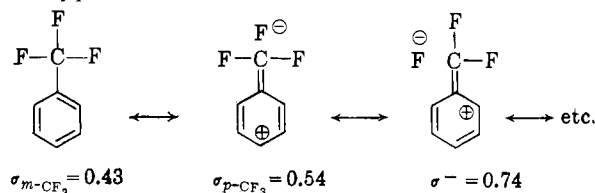
There do not appear to be enough experimental data available to show whether compounds with two or more amino groups attached to the same carbon atom are stabilized significantly by double bond-no bond resonance. Chang and Westrum have given thermochemical data on hexamethylenetetramine, a compound in which such resonance might be expected, and adamantane, the required hydrocarbon reference compound.³¹ These data are on the solid materials, however, and heats of vaporization would have to be estimated. More important, there do not appear to be enough accurate thermochemical data on simple amines to tell what differences in heats of formation between corresponding amines and hydrocarbons would be expected in the absence of resonance.

Fluorine and alkoxy substituents are unusual in that they are rather effective at both no-bonding and sharing electron pairs to form a double bond. Double bond-no bond resonance interaction between two different groups, X and Y, attached to the same carbon atom may be particularly strong when one group (*e.g.*, X) is highly electronegative and the other is particularly effective at supplying electron pairs to an electron-deficient center

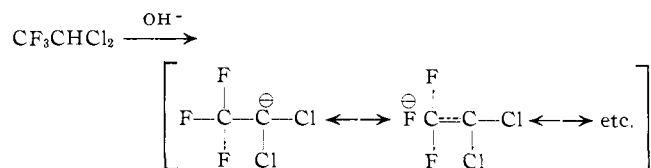


even though there may be only two important contributing resonance structures (I and II) instead of the three that contribute when X and Y are identical.

Resonance of this type has been suggested before. Roberts, Webb, and McElhill explained their observation that the Hammett for *p*-trifluoromethyl is larger than that for *m*-trifluoromethyl in terms of resonance of the type shown below.³²



Hammer and Matsen had previously discussed the ultraviolet spectra of benzyl chloride, benzal chloride, and benzotrichloride in terms of such resonance.³³ Miller, Frass, and Resnick³⁴ and others³⁵ have explained the carbanion-stabilizing effect of β -fluoro substituents in terms of no-bond resonance involving fluorine.



There do not appear to be enough thermochemical data to permit a reasonable estimate of the resonance energy due to no-bonding of allyl or benzyl fluorine atoms.

The fact that, relative to α -chloro substituents, α -fluoro substituents decrease the $\text{S}_{\text{N}}1$ reactivity of benzotrihalides but increase that of trihalomethyl anions has been rationalized in terms of double bond-no bond resonance elsewhere, as has the fact that two α -chloro substituents increase the solvolysis rate of vinyl

(31) S.-S. Chang and E. F. Westrum, Jr., *J. Phys. Chem.*, **64**, 1547 (1960).

(32) J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950).

(33) W. F. Hammer and F. A. Matsen, *ibid.*, **70**, 2482 (1948).

(34) W. T. Miller, Jr., W. Frass, and P. R. Resnick, *ibid.*, **83**, 1767 (1961).

(35) J. Hine, R. Wiesboeck, and R. G. Ghirardelli, *ibid.*, **83**, 1219 (1961).

chloride 500-fold but decrease that of chloromethyl methyl ether more than 2500-fold.³⁶

Double bond-no bond resonance may also explain the fact that α -fluoro substituents specifically increase the reactivity of methyl bromide derivatives toward methoxide ions relative to their reactivity toward iodide ions.³⁷ Bunnett has interpreted this observation in

(36) J. Hine and R. J. Rosscup, *J. Am. Chem. Soc.*, **82**, 6115 (1960).

terms of London forces,³⁸ but such an interpretation seems to demand that hydrogen be at least as much more polarizable than fluorine as chlorine is.

Acknowledgment.—The author should like to acknowledge his indebtedness to the National Science Foundation for a grant in support of this investigation.

(37) J. Hine, C. H. Thomas, and S. J. Ehrenson, *ibid.*, **77**, 3886 (1955).

(38) J. F. Bunnett, *ibid.*, **79**, 5969 (1957).

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, AMERICAN CYANAMID CO., BOUND BROOK, N. J.]

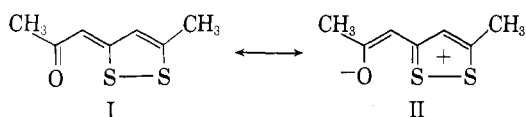
The 1,2-Dithiolium Cation. IV.¹ Conversion of the Dithiolium to the Thiothiophthene No-Bond Resonance System²

BY ERWIN KLINGSBERG³

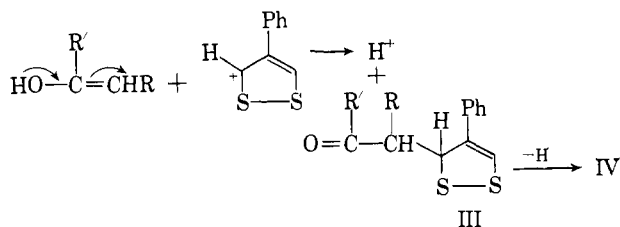
RECEIVED JUNE 8, 1963

Thiothiophthene derivatives (V) are conveniently prepared by the condensation of 4-phenyl-1,2-dithiolium hydrogen sulfate with methyl and methylene ketones to give IV, followed by treatment with P₂S₅. Chemical evidence of the "no-bond resonance" phenomenon in V is described.

4-Phenyl-1,2-dithiolium salts⁴ condense smoothly with methyl and methylene ketones. The structure of the products (IV) is shown by analysis, molecular weight determination, and the lack of infrared absorption in the 1,660 cm.⁻¹ carbonyl region. The dimethyl analog I is known to be similar in this respect⁵ and is also anomalous in its n.m.r. spectrum, showing no lines of normal shift for COCH₃ protons.⁶ The absence of ketonic character in I and IV can be rationalized in terms of a highly polarized dithiolium enol betaine structure (*e.g.*, II); analogous polarization evidently accounts for the observation by Tarbell and Hoffman that 1,4-thiapyrone and its derivatives are lacking in infrared carbonyl absorption.⁷



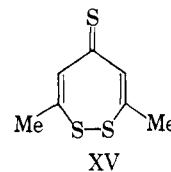
This condensation reaction presumably proceeds by attack of the electrophilic dithiolium cation on the enol or anionoid form of the carbonyl component; the adduct III is then dehydrogenated to the fully conjugated IV at the expense of additional dithiolium salt, which is used in excess to give yields of 40–50% based on ketone. The mild oxidizing action of dithiolium salts was earlier observed in the condensation with tertiary aromatic amines.⁸ Analogous condensations followed by dehydrogenation are known in the pyridinium series.⁹



We speculated that, for stoichiometric or mechanistic reasons, α -haloketones might afford superior results, but an experiment with phenacyl bromide gave no product.

Compounds IV are inert to carbonyl reagents such as phenylhydrazine and alkylating agents such as dimethyl sulfate, but react smoothly with phosphorus pentasulfide. The products V, readily obtained in good yield, are derivatives of the recently discovered thiothiophthene "no-bond resonance" system, which now becomes conveniently accessible in two steps from readily obtainable dithiolium salts. Preparative details for the few known thiothiophthene derivatives are scarce in the literature. The dimethyl compound XIVa was originally obtained from diacetylacetone (XIIIa) and P₂S₅ in 40% yield,¹⁰ but our results have been much poorer, and very recently a 15% yield has been reported.¹¹ We have also found the conversion of dibenzoylacetone (XIIIb) to XIVb¹² to be poor for preparative purposes.

Thiothiophthene no-bond resonance was discovered by X-ray analysis,¹³ which showed that the three sulfur atoms in the reaction product of diacetylacetone and phosphorus pentasulfide are collinear and equally spaced at 2.36 Å. distance, compared to the normal RS–SR bond distance of 2.04 Å. These results are incompatible with the cyclic disulfide structure XV



originally proposed for the compound,¹⁰ but can be explained in terms of two equivalent resonating structures (XIVa). Nuclear magnetic resonance spectroscopy has provided confirmatory evidence,⁶ but relatively little is known of the chemistry of the system. The accessibility of unsymmetrically substituted thiothiophthenes (V) from dithiolium salts has now made possible a chemical demonstration of no-bond resonance. Like normal thiocarbonyl compounds, Va

(9) F. Kröhnke and K. Ellegast, *Ann.*, **600**, 176 (1956); F. Kröhnke and I. Vogt, *ibid.*, **600**, 211, 228 (1956).

(10) F. Arndt, P. Nachtwey, and J. Pusch, *Ber.*, **58**, 1633 (1925).

(11) G. Pfister-Guillouzo and N. Lozac'h, *Bull. soc. chim. France*, 153 (1963).

(12) G. Traverso, *Ann. chim. (Rome)*, **44**, 1018 (1954).

(13) S. Bezzi, M. Mammi, and C. Garbuglio, *Nature*, **182**, 247 (1958).

(1) Paper III: E. Klingsberg, *J. Org. Chem.*, **28**, 529 (1963).

(2) Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(3) University of the City of New York, New York 31, N. Y.

(4) E. Klingsberg, *J. Am. Chem. Soc.*, **83**, 2934 (1961).

(5) G. Guillouzo, *Bull. soc. chim. France*, 1316 (1958).

(6) H. G. Hertz, G. Traverso, and W. Walter, *Ann.*, **625**, 43 (1959).

(7) D. S. Tarbell and P. Hoffman, *J. Am. Chem. Soc.*, **76**, 2451 (1954); C. G. Price and O. O. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, p. 22.

(8) E. Klingsberg and A. M. Schreiber, *J. Am. Chem. Soc.*, **84**, 2941 (1962).