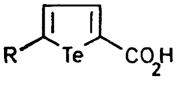
Electronic Transmission of Substituent Effects through the Tellurophen Ring

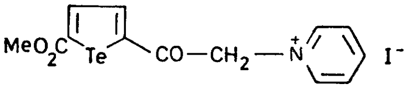
By **F. Fringuelli, G. Marino,* and A. Taticchi,** Istituto di Chimica Organica, Università di Perugia, Via Elce di Sotto 10, 06100 Perugia, Italy

The ionization constants of some 5-substituted tellurophen-2-carboxylic acids in water at 25 °C have been determined potentiometrically. An excellent linear correlation is obtained when the pK_a values are plotted against the σ_p constants. The ρ value (+1·20) is equal, within experimental error, to those for the thiophen and selenophen series, showing that the intensity of transmission of the electronic effects of substituents is substantially the same in the three heteroaromatic systems.

CONTINUING our studies of tellurophen,[1,2] we report a comparison of the sensitivity to substituent effects of this ring with those of the congener five-membered systems in the ionization of carboxylic acids. Acids (1)—(3) were available.[2] The 2,5-dicarboxylic acid (4) (which provides two points in the Hammett plot by its first and second ionization constants) was made by treatment of methyl 5-acetyltellurophen-2-carboxylate with iodine and pyridine[3] and subsequent alkaline hydrolysis of the pyridinium iodide (5). The dicarb-



(1) R = H
(2) R = Me
(3) R = Ac
(4) R = CO_2H



(5)

---

[1] F. Fringuelli, G. Marino, G. Savelli, and A. Taticchi, *J.C.S. Chem. Comm.*, 1971, 1441.

[2] F. Fringuelli and A. Taticchi, *J.C.S. Perkin I*, 1972, 199.

[3] L. Carroll King, *J. Amer. Chem. Soc.*, 1944, **66**, 894.

oxylic acid was obtained in satisfactory yield and was isolated, purified, and characterized through its dimethyl ester. Its structure was assigned from the n.m.r. and i.r. spectra. A previous attempt to prepare (4) from the methyl ester of acid (3) by the halogenoform reaction was unsuccessful. Likewise unsuccessful were all the attempts to prepare the bromo- and nitro-carboxylic acids through direct substitution of the unsubstituted acid or its methyl ester.

The thermodynamic pK_a values of acids (1)—(4) in water at 25 °C, determined potentiometrically, are in Table 1.

TABLE 1

Ionization constants of substituted tellurophen-2-carboxylic acids

Substituent	pK_a^T	Substituent	pK_a^T
H	3·97 ± 0·01	CO_2H	3·11 ± 0·02
Me	4·16 ± 0·01	CO_2^-	4·24 ± 0·02
Ac	3·36 ± 0·02		

Application of the Hammett Equation.—In applying the Hammett equation to heteroaromatic systems two procedures can be adopted.[4] (1) The same ρ value is used for the same reaction of all the aromatic nuclei (*e.g.*, $\rho = 1$ for the ionization of carboxylic acids in water at 25 °C) and new σ constants are calculated for each substituent, depending on the nature of the ring and the relative position with respect to both the reaction centre and the heteroatom. (2) The conventional σ_m and σ_p constants, derived from benzene chemistry, are used and separate reaction constants ρ are calculated for the reactions at each different ring. The latter procedure is the more used in correlating the reactivities of five-membered rings [5] and has been adopted by us.

The linear plot constructed by plotting log K/K_0 for the 5-substituted tellurophen-2-carboxylic acids against the σ_p constants [6] is excellent † (Figure). The ρ values for the ionization of the 2-carboxylic acids of all the congener rings are summarized in Table 2. The ρ value for the thiophen nucleus has been recalculated by use of the pK_a values of the substituted thiophencarboxylic acids determined by Butler,[7] and is larger than the value reported by Imoto and his co-workers.[8]

TABLE 2

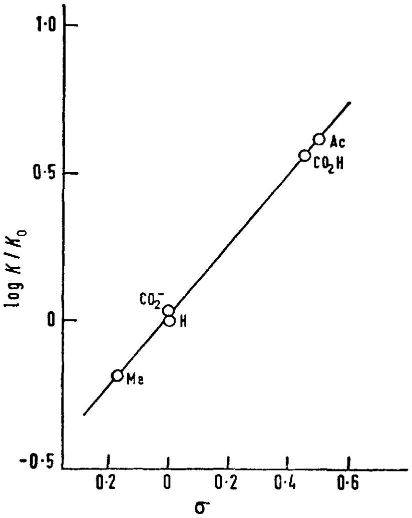
Application of the Hammett equation to 5-membered heteroaromatic congeners

pK_a In water at 25 °C	ρ [a]	r [b]	s [c]	n [d]	Ref.
2-Furoic acids	1·40	0·988	0·06	6	*e*
Thiophen-2-carboxylic acids	1·20	0·980	0·050	7	7
Selenophen-2-carboxylic acids	1·23	0·998	0·02	7	*f*
Tellurophen-2-carboxylic acids	1·20	0·999	0·013	5	*g*

[a] Reaction constant. [b] Correlation coefficient. [c] Standard deviation from the regression line. [d] Number of acids entering into the determination of ρ. [e] W. E. Catlin, *Iowa State Coll. J. Sci.*, 1935, **10**, 65. [f] D. Spinelli, G. Guanti, and C. Dell'Erba, *Ricerca Sci.*, 1968, **38**, 1048. [g] This work.

The furan ring exhibits the highest sensitivity to structural changes ($\rho = 1·4$); thiophen, selenophen, and tellurophen behave similarly, the ρ value being the same within experimental error.

More information could be obtained from the calculation of the σ constants by applying method (1) (see before) and comparison with the values calculated by Dewar and Grisdale's procedure,[9] but the necessary geometrical and polarizability parameters for the tellurophen ring are not available. Comparison with the pyrrole nucleus (for which $\rho = 1·65$ [10]) is of uncertain significance, since nitrogen belongs to a different Periodic Group: further, reactions of pyrrole can be complicated by intramolecular hydrogen bonding in the carboxylate anion.



Hammett plot for the ionization of substituted tellurophen-2-carboxylic acids in water at 25 °C

Substituent Constants for the Heteroatoms.—The heteroatoms can be considered [4] as ' substituents ' and the σ constants for the replacement of a CH=CH moiety in the benzene ring by O, S, Se, and Te atoms can easily be calculated from the ionization constants of the unsubstituted acids. The observed sequence in σ_α values (Table 3) appears to be a function of the electronegativity of the heteroatoms.

TABLE 3

' Substituent constants ' for the heteroatoms [a]

Atom	σ_α	Electronegativity [b]
O	1·04	3·6
S	0·67	2·5
Se	0·60	2·4
Te	0·23	2·1

[a] $\sigma_\alpha = pK_0 - pK_a$, where pK_0 is 4·20 and pK_a are: 3·16 (2-furoic acid: P. O. Lumme, *Suomen Kem.*, 1960, *B*, **33**, 87); 3·53 (thiophen-2-carboxylic acid: ref. 7); 3·60 (selenophen-2-carboxylic acid: ref. *f* of Table 2); and 3·97 (tellurophen-2-carboxylic acid).

---

† The K_1 and K_2 constant for the ionization of the 2,5-dicarboxylic acid have been corrected for the statistical factor.

[4] H. H. Jaffe and H. L. Jones, *Adv. Heterocyclic Chem.*, 1964, **3**, 236.

[5] G. Marino, *Adv. Heterocyclic Chem.*, 1971, **13**, 298.

[6] D. M. McDaniell and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

[7] A. R. Butler, *J. Chem. Soc.* (*B*), 1970, 867.

[8] E. Imoto, R. Motogama, and H. Kakiuchi, *Nippon Kagaku Zasshi*, 1956, **77**, 812.

[9] M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3539.

[10] F. Fringuelli, G. Marino, and G. Savelli, *Tetrahedron*, 1969, **25**, 5815.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 instrument and n.m.r. spectra with a Varian A-100 instrument. τ Values are relative to internal tetramethylsilane in $CDCl_3$ at room temperature. Acids (1)—(3) were prepared as reported.[2]

Dimethyl Tellurophen-2,5-dicarboxylate.—Iodine (2·85 g) in dry pyridine (10 ml) was added to methyl 5-acetyltellurophen-2-carboxylate (3 g) dissolved in dry pyridine (40 ml). The solution was kept at room temperature for 15 min, then was heated at 60 °C for 90 min and at 80 °C for 120 min. The mixture was then left overnight at room temperature. The excess of pyridine was removed under reduced pressure and the solid residue was treated several times with ethyl ether to remove the unchanged starting material. About 1 g of methyl 5-acetyltellurophen-2-carboxylate was recovered. Ethanol–water (6 : 4; 90 ml) and sodium hydroxide (8·3 g) were added to the residue and the mixture was heated under reflux for 2 h. The resulting solution was washed with ether and the mother liquor was acidified with dilute H_2SO_4. The precipitate was extracted with ether (500 ml) and the ether solution washed with saturated brine, dried (Na_2SO_4), and evaporated *in vacuo*. The residue (1·2 g) was treated with an ethereal solution of diazomethane and, after evaporation of the solvent, the residue was crystallized from ligroin to give 0·9 g of the *diester* as sole product on t.l.c. analysis with m.p. 101—102 °C (Found: C, 32·6; H, 2·8. $C_8H_8O_4Te$ requires C, 32·5; H, 2·7%).

The n.m.r. spectrum shows two singlets at τ 6·15 (CO_2Me) and 1·47 (β-protons) integrated for six and two protons respectively. The chemical shifts are in good agreement with those observed in other derivatives of tellurophen.[2] The $\nu_{max.}$ of the i.r. spectrum (in CCl_4) are at 2955, 1725, 1708, 1435, 1265, 1240, and 1070 cm^{-1}. The doublet in the 1700 cm^{-1} region is probably the result of a conformational isomerism, similar to that observed in the 2-carbonyl derivatives of furan and thiophen.[11]

Tellurophen-2,5-dicarboxylic Acid (4).—A solution of dimethyl tellurophen-2,5-dicarboxylate (0·5 g) in 95% ethanol (22 ml) and N-sodium hydroxide (10 ml) was heated under reflux for 2 h. After cooling the solution was washed with ether and the aqueous layer was acidified with dilute H_2SO_4. The precipitate was filtered off and crystallized from water to give 0·285 g of the *diacid*, m.p. *ca.* 308 °C (decomp.) (Found: C, 27·1; H, 1·5. $C_6H_4O_4Te$ requires C, 26·9; H, 1·5%).

Dissociation Constants.—Dissociation constants were determined by potentiometric titration at 25 ± 0·05 °C in water. A Metrohm 388 pH-meter and a combined electrode EA 121 X were used. The procedure was that previously described.[12] The initial acid concentrations were *ca.* 1·5—2·0 × 10^{-3}M. The pK_a values were calculated by the method described by Albert and Sargent.[13] With tellurophen-2,5-dicarboxylic acid analysis by Noyes's method [13,14] was used in order to overcome difficulties arising from the insufficient separation of the pK_a values for the first and the second ionizations.

We thank the C.N.R., Rome, for financial support.

[2/683 *Received*, 22nd *March*, 1972]

---

[11] D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Chem. Comm.*, 1971, 625.

[12] F. Fringuelli, G. Marino, and A. Taticchi, *J. Chem. Soc.* (*B*), 1970, 1595.

[13] A. Albert and E. P. Sargent, ' Ionization constants of acids and bases,' Methuen, London, 1962, p. 28.

[14] A. A. Noyes, *Z. phys. Chem.*, 1893, **11**, 495.