thallium triacetate is very specific in the cleavage reaction and high yields of a single product are observed. We also wish to present evidence in support of a two-step mechanism in which both steps proceed at similar rates. Winstein[2] has reported that thallic triacetate oxidizes cyclohexene and has probed the mechanism of the reaction and stereochemistry of the products.

Phenylcyclopropane is cleaved by thallium triacetate in acetic acid at 75°. In a typical reaction, a solution that was 0.04 M in thallium triacetate and 0.08 M in phenylcyclopropane was allowed to react for 120 hr. The sole products are 1-phenyl-1,3-diacetoxypropane and trans-cinnamyl acetate which are obtained in 92% and 8% yields, respectively. The 1-phenyl-1,3-diacetoxypropane was collected and identified by its n.m.r. spectrum. No 2-phenyl-1,3-diacetoxypropane was found. The trans-cinnamyl acetate was identified by its v.p.c. retention times on XF-1150 (cyano silicone), QF-1 (fluoro silicone), and SF-96. In the previous work the trans-cinnamyl acetate was identified by its n.m.r. and infrared spectra.
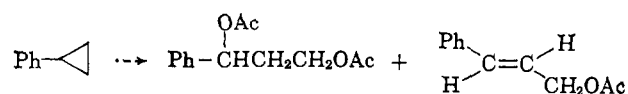
Ethyl cyclopropane was subjected to similar reaction conditions. The ratio of 1,3-diacetoxypentane to 2-ethyl-1,3-diacetoxypropane is approximately 65. Both products were readily separable on Degs and XF-1150. Less than 5% of the reaction product consists of lower molecular weight material (unsaturated monoacetates). By contrast the ratio of 1,3-diacetoxypentane to 2-ethyl-1,3-diacetoxypropane in the lead tetraacetate reaction is 6.

The stereochemistry of the reaction has been examined with norcarane. Norcarane is cleaved to give 2-acetoxymethylcyclohexyl acetate and 1,3-diacetoxycycloheptane in the ratio of 15 to 1. Approximately 5% of the reaction product is of lower molecular weight. By contrast the corresponding ratio in the lead tetraacetate cleavage is 5.3 to 1. The n.m.r. spectrum of the 2-acetoxymethylcyclohexyl acetate was examined to determine the stereochemistry of this product. A sharp singlet at τ 8.10 corresponding to the six hydrogens of the two acetate groups is observed for the trans isomer.[4] The cis isomer[4] shows two sharp singlets at τ 8.10 and 8.03. Each singlet corresponds to three hydrogens. The signal at τ 8.03 must correspond to the predominantly axial acetoxy group in the cis isomer. The reaction product has a sharp singlet at τ 8.10. The cis isomer could be detected if it were present to the extent of 2% of the reaction mixture. Thus the cleavage reaction stereospecifically yields the trans ring-opened product.

The cleavage reaction can be carried out conveniently with thallic oxide. Under the reaction conditions, thallic oxide is converted to thallium triacetate. This modification avoids the use of the moisture-sensitive thallium triacetate.
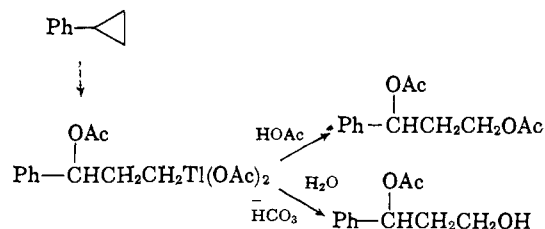
That the reaction with thallium triacetate is a two-step process is indicated by the following observations.

(2) C. B. Anderson and S. Winstein, J. Org. Chem., **28**, 606 (1963).

(3) Liquid phases obtained from Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

(4) The authors wish to thank Dr. Lloyd Dolby for authentic samples of cis- and trans-2-acetoxymethylcyclohexyl acetate.

Aliquots of the reaction mixture of phenylcyclopropane and thallium triacetate were quenched in water at various time intervals. Each sample was extracted with ether and the ethereal solution was washed with sodium bicarbonate. Analysis by v.p.c. showed the presence of a third product of longer retention time than the diacetate. Acetylation of the reaction mixture removes this product and increases the yield of 1-phenyl-1,3-diacetoxypropane. The product is an alcohol which results from the decomposition of the organothallium intermediate under the work-up conditions. As the reaction proceeds the peaks cor-

responding to the alcohol and diacetate increase while the phenylcyclopropane decreases. The alcohol peak is initially larger than the diacetate peak but decreases with time to a small value. This strongly suggests, that the reaction involves a two-step mechanism, the first step of which is the formation of the organothallium intermediate. The second step is the decomposition of the intermediate. Both steps proceed at measurable rates.

By analogy it appears that the reaction with lead tetraacetate involves an organolead intermediate which decomposes very rapidly and the rate-determining step is the cleavage of the cyclopropane ring. Under similar reaction conditions the attack of mercuric acetate on cyclopropanes would be expected to give stable organomercury compounds. The reaction with mercuric acetate has been observed by Levina.[5–8]

Further work on the direction of cleavage, stereochemistry of cleavage, and elucidation of the mechanism of cleavage by rate studies is in progress.

(5) R. Ya. Levina and V. N. Kostin, Zh. Obshch. Khim., **23**, 1054 (1953).

(6) R. Ya. Levina and V. N. Kostin, Dokl. Akad. Nauk. SSSR, **97**, 1027 (1954).

(7) R. Ya. Levina, V. N. Kostin, and V. A. Tartakouskii, Zh. Obshch. Khim., **27**, 881 (1957).

(8) R. Ya. Levina, V. N. Kostin, and V. A. Tartakouskii, ibid., **24**, 2998 (1956).

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The Electrochemical Oxidation of Formic Acid in the Presence of Dimethylformamide

Sir:

Conway and Dziechiuch[1] have shown that the electrolysis of potassium formate in formic acid gives carbon dioxide and hydrogen, according to the following over-all electrode reactions

$$HCOO^- \longrightarrow CO_2 + H^+ + 2e$$

$$2H^+ + 2e \longrightarrow H_2$$
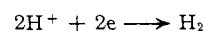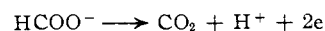
with the coulombic yield approaching 1 mole of CO_2

(1) B. E. Conway and M. Dziechiuch, Can. J. Chem., **41**, 21 (1963).

and 1 mole of H_2 per 2 faradays.[2] The sole anodic product is CO_2 and H_2 is formed only at the cathode. We find that when potassium formate (5 g.) in $98+\%$ formic acid (60 ml.) is electrolyzed at $20°$ at 0.40 amp. (1 cm.[2] platinum electrodes at a separation of 0.6 cm.) the rate of total gas production is 99.1–99.6% of that predicted by the above mechanism.

The addition of dimethylformamide effects profound changes in the course of the reaction. The rate of total gas production for a system containing potassium formate (4.2 g.) in formic acid (55 ml.) and dimethylformamide (5 ml.), after 240 min. of electrolysis, was 60.7% of the normal rate, with the gas formed being 82.7% H_2. With more dimethylformamide (4.2 g. of HCOOK, 40 ml. of HCOOH, 20 ml. of DMF) the rate of gas evolution is further decreased, being 53.3% (94.1% H_2) of normal after 108 min. and 56.6% (88.7% H_2) of normal after 1248 min. In both cases the remaining gas is almost entirely CO_2.

Two compounds, N-methyl-N-formyloxymethylformamide (I) and 2,6-diformyl-2,6-diaza-4-oxaheptane (II), have been isolated from these electrolyses. From a solution of 4.2 g. of HCOOK in 40 ml. of $98+\%$ HC-

I

II
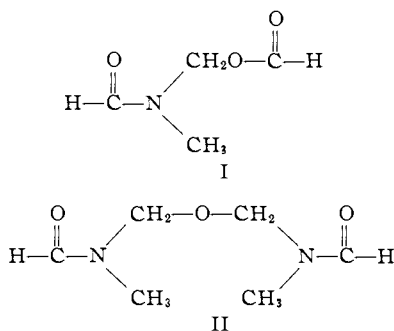
OOH and 18.9 g. of DMF, electrolyzed for 22.6 hr. at 0.40 amp., it was possible to obtain 9.9 g. (33%) of I and 4.3 g. (20.9%) of II. Under more anhydrous conditions (3.4 g. of HCOONa in 40 ml. of HCOOH, dried over $MgSO_4$ and distilled, and 18.9 g. of DMF electrolyzed for 23.7 hr.) it was shown by v.p.c. analysis that 51.4% of the DMF was converted to I and 35.4% of the DMF remained unreacted. On distillation this reaction mixture yielded 13.3 g. (44.2%) of I and 1.74 g. (8.4%) of II.

In the electrolysis of acetate ion, the over-all electrode reactions are[3]

$$2CH_3COO^- \longrightarrow 2CO_2 + C_2H_6 + 2e$$

$$2H^+ + 2e \longrightarrow H_2$$

with the coulombic yield in acetic acid approaching 2 moles of CO_2, 1 mole of H_2, and 1 mole of C_2H_6 per 2 faradays.[4] When potassium acetate (5 g.) in acetic acid (60 ml.) is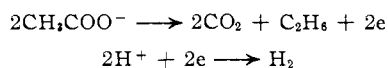 electrolyzed as above, the rate of total gas production is $100 \pm 1\%$ of that demanded by the above equations, with the ratio, $CO_2:C_2H_6$, varying from 1.99 to 2.02. Traces of methane are also present in the gas mixture.

When 30 ml. of the acetic acid is replaced with dimethylformamide, the rate of total gas evolution is

(2) K. Hopfgartner, *Monatsh.*, **32**, 523 (1911); F. Müller, *Z. Electrochem. angew. physik. chem.*, **33**, 173 (1927); E. Baur, *Helv. Chim. Acta*, **11**, 372 (1928).

(3) B. C. L. Weedon, *Quart. Rev.* (London), **6**, 380 (1952).

(4) C. L. Wilson and W. T. Lippincott, *J. Am. Chem. Soc.*, **78**, 4290 (1956).

69.1% of normal after 2 hr. of electrolysis and 81.5% of normal after 24 hr. of electrolysis. Again it is the anodic gassing that has been suppressed, and that anodic gas which is formed still shows a $CO_2:C_2H_6$ ratio of almost exactly 2. The rate of methane production is almost identical with that observed in the absence of dimethylformamide, and the total methane produced is approximately 0.005 mole. After 31.6 hr. of electrolysis it was possible to isolate 3.6 g. of N-acetoxymethyl-N-methylformamide, III.

III
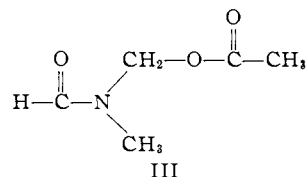
This known ester-amide[5] III (b.p. 66–67° at 0.3 mm.; $n^{24}D$ 1.4420; $\gamma_{C=O}$ 5.79 and 5.97 μ. *Anal.* Calcd. for $C_5H_9O_3N$: C, 45.80; H, 6.92; N, 10.68. Found: C, 45.90, 45.90; H, 6.79, 6.84; N, 10.67, 10.66) was prepared in 96% yield by acetylating N-hydroxymethyl-N-methylformamide.

The structure of I (b.p. 44–45° at 0.005 mm.; $n^{24}D$ 1.4471) is indicated by comparison of its infrared spectrum ($\gamma_{C=O}$ 5.83 and 5.97 μ) with that of III, by its analysis (*Anal.* Calcd. for $C_4H_7O_3N$: C, 41.03; H, 6.03; N, 11.96. Found: C, 41.16, 41.16; H, 6.11, 6.12; N, 11.84, 11.76) and by its reaction with β-naphthol to give the known methyl-(2-hydroxynaphthylmethyl)amine hydrochloride, m.p. 205–206° dec., in high yield.[6]

The ether II, m.p. 63–64.5°, showed no depression on mixture melting with a sample prepared by a known method.[7]

In both systems the first step is a one-electron transfer at the anode to form an acyloxy radical, which then abstracts a hydrogen atom from dimethylformamide. In acetic acid the hydrogen atom abstraction must have been effected largely by the acetoxyl radical, since the total methane produced is far less than the amount of III isolated. In the formate case the only reasonable possibility is for the hydrogen atom ab-

$$RCOO^- \longrightarrow RCOO\cdot + e$$
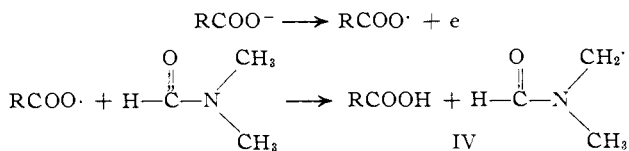
straction to be effected by the formyloxy radical. These results thus demonstrate, for the first time, that the electrochemical oxidation of formic acid involves single-electron transfers at the anode rather than a concerted two-electron transfer, and that the acetoxyl and formyloxy radicals, when generated at an electrode surface, are species of some finite lifetime and are capable of entering into reaction with a suitable substrate.

The subsequent product-forming steps are less certain. The esters I and III could result from the combination of acyloxy radicals with IV and with

(5) G. Sosnovsky, *J. Org. Chem.*, **28**, 2934 (1963).

(6) W. J. Burke, M. J. Kolbezen, and C. W. Stephens, *J. Am. Chem. Soc.*, **74**, 3601 (1952); H. Böhme, A. Dick, and G. Driesen, *Chem. Ber.*, **94**, 1879 (1961).

(7) J. H. Robson and J. Reinhart, *J. Am. Chem. Soc.*, **77**, 2453 (1955).

the ether II resulting from hydrolysis of I which may be shown to be very facile. Alternatively, the radical IV might discharge another electron at the anode to give the carbonium ion V, which could then react with solvent to give I and III or with water to give N-hydroxymethyl-N-methylformamide, the probable precursor of II.

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On the Numerical Integration of Rate Equations

Sir:

A recent publication[1] by Schaad describes a Monte Carlo method, of considerable generality, for the integration of kinetic rate equations whose analytical solutions are intractable or nonexistent. It is the purpose of this communication to point out that "direct" numerical methods[2,3] are usually to be preferred because of their much greater speed, greater accuracy, and equal ease of programming. In particular, the fourth-order Runge–Kutta method[3,4] is very convenient for kinetic problems. This method, while roughly half as fast as more efficient methods, has for kinetic work the advantages of being self-starting, not requiring integration at equally spaced values of time, and being readily available as a library routine at most computer installations.

A general chemical reaction scheme may be specified by a set of equations of the form

$$\frac{dC_i}{dt} = F_i(t, T, C_0 \ldots \ldots C_n) \qquad (1)$$

$$i = 0, 1, \ldots, n$$

where C_i is the concentration of the ith reacting species, and the F_i, functions of time, temperature, and concentrations of all species. It is precisely systems of this type which may be integrated directly, for specific initial conditions, by the Runge–Kutta method. Temperature will usually enter F_i only as a parameter, but if it is a nonconstant function of time (or indeed of any of the concentrations), the method is still applicable; hence nonisothermal problems, to which the Monte Carlo method is unsuited, may be treated.

As an example, the system treated by Schaad[1]

$$A \xrightarrow{k_1} B + C \xrightarrow{k_2} D \qquad (2)$$
$$\underset{k_3}{\underline{\qquad\qquad\qquad}}$$

(1) L. J. Schaad, *J. Am. Chem. Soc.*, **85**, 3588 (1963).
(2) L. Fox, "Numerical Integration of Ordinary and Partial Differential Equations," Pergamon Press, New York, N Y., 1962.
(3) A. Ralston and H. S. Wilf, "Mathematical Methods for Digital Computers," John Wiley and Sons, Inc., 1960, Chapters 8 and 9.
(4) S. Gill, *Proc. Cambridge Phil. Soc.*, **47**, 96 (1951).

which gives, for $B(0) = C(0)$ the system

$$\frac{dA}{dt} = -(k_1 + k_3)A$$

$$\frac{dB}{dt} = k_1 A - k_2 B^2 \qquad (3)$$

$$\frac{dD}{dt} = k_3 A + k_2 B^2$$

was integrated with $k_1 = 1$, $k_2 = 0.5$, $k_3 = 0.2$ from the initial condition $A(0) = 2$, $B(0) = C(0) = D(0) = 0$ (all units arbitrary). The integration was carried out from $t = 0$ to $t = 5$ with a step of 0.1, results agreeing with the exact solution given by Pearson, King, and Langer[5] to five figures throughout. This required approximately 2.5 sec. on a Ferranti Mercury computer, $1/_{500}$ of the time required for the Monte Carlo method on a computer of similar speed.[6]

Using the Runge–Kutta method, it is possible and practicable to determine rate constants by adjusting trial values until the solution of the differential equations agrees as well as possible with experimental measurements. For a least-squares determination, one has to minimize the quantity

$$D = \sum_i \sum_j w_{ij}(\Delta_{ij})^2 \qquad (4)$$

where Δ_{ij} is the difference between the calculated and experimental concentrations of the ith species at the jth experimental point. The w_{ij} are weights assigned to compensate for differences in magnitude of the various concentrations and differences of precision among the various measurements. In particular, if the kth species is not measured in the experiment, $w_{kj} = 0$ for all j.

Two procedures which have been found suitable for the minimization of D with respect to the rate constants are those devised by Rosenbrock[7] and Fletcher and Powell.[8] The latter has more rapid convergence but requires the evaluation of the partial derivatives of D with respect to the various rate constants. These in turn require calculation of the partial derivatives of the calculated concentrations with respect to the rate constants at all experimental points, giving rise to further differential equations which must be integrated simultaneously with the rate equations.

To illustrate these processes, both were used to extract the original k's from the values, obtained above, of B as a function of t. These values were rounded to three figures and regarded as "experimental data." Two starting approximations to the k values were used; the first, $k_1 = 0.95$, $k_2 = 0.47$, $k_3 = 0.25$, was obtained graphically from the B vs. t data; the second was taken five times poorer, viz., $k_1 = 0.75$, $k_2 = 0.35$, $k_3 = 0.45$. All weights were taken equal to unity.

The Rosenbrock method gave the final result $k_1 = 1.0000$, $k_2 = 0.5001$, $k_3 = 0.1997$, standard deviation $= 2.6 \times 10^{-4}$, from both starting approximations. From the better approximation, this required 143 integrations of the rate equations, and from the poorer

(5) R. G. Pearson, L. C. King, and S. H. Langer, *J. Am. Chem. Soc.* **73**, 4149 (1951).
(6) The Monte Carlo method required 11 min. on an IBM-7072.
(7) H. H. Rosenbrock, *Computer J.*, **3**, 175 (1960).
(8) R. Fletcher and M. J. D. Powell, *ibid.*, **6**, 163 (1963).