nolysis in dilute alkali at pH 9 yielded the oily cyclopropyl aldehyde (VIIIA) [IR cm^{-1}: 1700, 1716; NMR: doublet (1H) $\tau = 0.20$, singlet (3H) $\tau = 8.57$, singlet (6H) $\tau = 8.95$]. Reaction of (IXA) with lithium carbonate and lithium chloride in anhydrous dimethylformamide gave quantitatively the crystalline cyclopropyl aldehyde (VIIIB), isomer of (VIIIA) [mp 56°; IR cm^{-1}: 1700, 1716; NMR: doublet (1H) $\tau = 0.54$, singlet 3H) $\tau = 8,60$, singlet (6H) $\tau = 9.00$]. The mass spectra of compound (VIIIA) and (VIIIB) were identical. Both (VIIIA) and (VIIIB) on treatment with 10% methanolic potassium hydroxide gave exclusively the hydroxy ketone (XI) which was oxidized with Jones' reagent to the diketone (XII) [mp 109°; IR cm^{-1}: 1724, 1750; NMR: singlet (1H) $\tau = 7.35$, singlet (1H) $\tau = 7.96$, singlet (2H) $\tau = 8.10$, singlet (3H) $\tau = 8.70$, singlet (6H) $\tau = 8.91$][4].

Zusammenfassung. Einfache photochemische Methode für die Substitution von α-H-Atomen eines α, β-ungesättigten Ketons durch eine Acetaldehyd-Seitenkette.

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Polarographic Determination of the Reaction Rate of the Second Step in an SN1 Displacement

We wish to disclose the first direct determination of the rate of the second 'very fast' step in an SNI displacement by a novel application of polarographic kinetic currents.

Since the discovery of polarographic kinetic currents[1] this method has been frequently used for the determination of fast reaction rates mainly in an 'equilibrium situation'.

$$N \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R \qquad (1)$$

If a nonreducible species N is in equilibrium with a reducible species R, then under certain conditions, which result in 'complete kinetic control', the polarographic wave of R is controlled by the rate of formation k_1 and the rate of decay k_2 of this species.

Equation (2) gives the value of the kinetic current $\bar{i}_k$ as a function of the concentration of N, the two rate constants k_1 and k_2, the diffusion constant of the reducible species D and the average surface of the electrode q[2–4].

$$\bar{i}_k = n \text{ F } 10^{-3}\, q\, D^{1/2}\, k_1 \sqrt{1/k_2}\, [\text{N}] \qquad (2)$$

Since equation (2) contains two unknowns (k_1 and k_2), we must have at our disposal a second relationship between them, in order to be able to solve the system. Such a relationship is mostly provided by the determination of the equilibrium constant $K = k_1 / k_2 = [R] / [N]$.

Consider now an irreversible system undergoing SN1 displacement.

$$RX \xrightarrow{k_1} R^{(+)} \xrightarrow{k_2} RS \qquad (3)$$

The starting material RX ejects the leaving groupX^- in the rate – determining first step and yields the carbonium ion $R^{(+)}$. This species reacts 'extremely rapidly' with the solvent S and yields the end product RS. The reaction is first order and the overall rate is identical with the rate of the first step k_1. Let us assume that both RX and RS are polarographically nonreducible and $R^{(+)}$ yields a well defined polarographic wave.

Equation (2) is immediately applicable to this system and may be written in the form (4)

$$\bar{i}_{k(t)} = n \text{ F } 10^{-3}\, q\, D^{1/2}\, k_1 \sqrt{1/k_2}\, [RX]_t \qquad (4)$$

The kinetic current of the carbonium ion, $\bar{i}_{k(t)}$ is directly proportional to the concentration of the starting material RX. Since RX decreases by a first order reaction, the kinetic current is time dependent and from this time dependence it is possible to evaluate simply the overall reaction rate k_{exp}.

Now the overall reaction rate k_{exp} is identical with the rate of the first step k_1.

Consequently, if we introduce into the equation (4) the kinetic current at time zero $\bar{i}_{ko}$ obtained by extrapolation, the initial concentration of the starting material $[RX]_o$ and substitute the known k_{exp} for k_1 the rate constant for the second fast step k_2 may be calculated.

Since diffusion coefficients are difficult to determine, it is convenient to eliminate from equation (4) the diffusion coefficient D by introducing the concept of 'theoretical diffusion current' $\bar{i}_d$. This may be defined as the height of the diffusion controlled polarographic wave given by a reducible compound which has the same diffusion coefficient as RX in the same solvent system and is present in the same concentration as RX. It is clear that $\bar{i}_d$ may be determined by recording a polarogram of a reducible compound of very approximately the same size and shape as RX. Thus, we obtain the equation (5) which contains besides k_2 only readily measurable quantities.

$$\bar{i}_{k_o} / \bar{i}_d = 0.886 \sqrt{[\text{drop time}]}\, k_{exp} / \sqrt{k_2} \qquad (5)$$

In acetone water mixtures which contain less than 10% v/v water the chloride I has been reported[5] to undergo an SN1 displacement and yield the alcohol III via the carbonium ion II.

We now find that this system gives a clear polarographic wave ($E_{1/2} = -0.37$ V vs S.C.E.) which decreases with time as a first order reaction. The wave is independent of mercury pressure[1], surfactants, linearly dependent on the concentration of I and it gives smooth '*i–t*' parabolas

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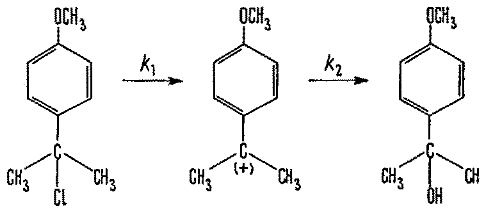
with and exponent ~ 0.70[6]. (Criteria of a fully rate controlled volume reaction). It can be rigorously concluded that the reducible species responsible for this polarographic wave is indeed the carbonium ion II. Only the starting chloride I, the carbonium ion II and the product III participate in the SN1 displacement. The product III is nonreducible and can not be responsible for the wave. Moreover, its concentration is growing with time whereas the polarographic wave is diminishing. Since the wave is fully rate controlled, it can not be due to the starting chloride I but must be due to a species produced from I by a chemical reaction. The carbonium ion II is thus the only candidate.



I II III

In agreement with this conclusion one may directly observe a beautifully developed one electron reduction wave of the carbonium ion II if one dissolves the alcohol III in sulphuric acid-water or sulphuric acid-acetic acid mixtures of extreme acidity ($E_{1/2} = -0.49$ V vs S.C.E. at $H_0 = -2$; $E_{1/2} = -0.40$ V vs S.C.E. in 6% sulphuric acid in acetic acid. The small differences in half wave potential are understandable in view of the large differences in solvent, ionic strength, and the resulting uncorrected diffusion potentials).

Consequently, we have concluded that we are indeed dealing with a case as discussed above and we proceeded with the evaluation of k_2 in the manner indicated. The decrease of the wave gave an excellent straight line fit in a first order plot from which k_{exp} was evaluated. The value of k_{exp} was independent of mercury pressure, surfactants and the concentration of I. The straight line plots also gave the values of $\bar{i}_{ko}$ for the individual concentrations of I. The value of $\bar{i}_d$ was determined from the known waves of acetophenone in the same medium. To insure sufficient conductivity around time zero (before more hydrochloric acid is formed) an initial concentration of hydrochloric acid 0.05 M was used. It was also ascertained experimentally that the changing concentration of hydrochloric acid had no influence on the magnitude of the limiting current of the wave which was measured and specifically that hydrochloric acid did not influence the current at the potential (-0.45 V vs S.C.E.) at which the readings of $\bar{i}_{k(t)}$ were made. In this manner the data assembled in the Table were obtained.

Values of k_1 and k_2 derived for the SN1 reaction of *p*-methoxy 2-phenyl propyl chloride

% H_2O (v/v)	$k_{exp} = k_1 s^{-1}$*	$\bar{i}_{ko}/\bar{i}_d$*	$k_2 s^{-1}$
5	9.2×10^{-3}	3.2×10^{-4}	2.0×10^3
7.5	10.5×10^{-3}	2.7×10^{-4}	3.9×10^3
8.7	12.4×10^{-3}	2.1×10^{-4}	8.6×10^3

*Data obtained at -0.45V vs S.C.E., drop time = 2.50 s, 25 °C.

The value of k_1 derived experimentally in this study is about six times smaller than that previously obtained by extrapolation from results at low temperatures and different water concentrations[5]. The increase of k_1 with increasing water concentration is only about half of that previously extrapolated[5]. In view of the higher concentrations of I (5% v/v) in our case and the fact that the previous study obtained the results by extrapolation, the two values of the overall rate constants can be considered compatible. As would be expected the value of k_2 increases more rapidly than k_1 with increasing water concentration. There is a difference of almost six orders of magnitude between the rate of the first and second step.

This example is the first case in which the rate of the second step of an SN1 displacement has been directly determined. Polarography is uniquely suitable for such a study, since relaxation techniques are only capable of studying equilibrium systems.

Zusammenfassung. Die Zeitabhängigkeit des polarographischen Stromes, welche man bei der gemäss SN1 verlaufenden Hydrolyse von *p*-Methoxy-2-phenylpropylchlorid beobachtet, ermöglicht die Bestimmung der Geschwindigkeitskonstanten k_1 der Gesamtreaktion sowie auch der Geschwindigkeitskonstanten k_2 des zweiten raschen Schrittes, welcher nach pseudo-erster Ordnung verläuft. Für k_2 ergibt sich in Aceton, das 5% Wasser enthält, bei 25 °C $k_2 = 2{,}0 \times 10^3$ sec^{-1}.

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[6] K. Wiesner, Colln Czech. chem. Commun. *12*, 64 (1947).

[7] We would like to thank the N.R.C. for provision of a grant to purchase the Electrochemical System and the University of New Brunswick for a Fellowship for one of us (D.B.).

A Defense Alkaloid in a Carnivorous Beetle

The common European ladybug *Coccinella septempunctata* L. (Coleoptera, Coccinellidae) has long been known to possess the chemical defenses that are expected to be associated with its aposematic coloration[1]. The insect, when molested, releases droplets of orange haemolymph at its articulations. This 'reflex bleeding' of Coccinellidae insures a relative immunity towards predators, especially ants[2].

In a preliminary study, 1600 *C. septempunctata* (collected in Brussels in December 1970) were blended at room temperature in methanol. The supernatant was separated by centrifugation and partitioned between methanol and