of the reactants. An exact expression even on the
basis of mechanism proposed by Noyes et al.9,10 is
difficult to obtain. However, on the basis of experi-
mental data $v$ and $T$ are found to be related as fol-
ows:

$$v = P \exp(-E/RT)$$  \hspace{1cm} (1)

where $P$ is a constant, $T$ is the absolute temperature.

Furthermore, $E$ is also a constant termed as the energy
of activation of frequency of oscillation and $R$ is
the usual gas constant. Rate constant $k$ for a
reaction is given by

$$k = A \exp(-E/RT)$$  \hspace{1cm} (2)

where $E$ is the energy of activation and $A$ is the
frequency factor. Using Eqs. (1) and (2), the
expression for the frequency, $v$, would be given by

$$v = \frac{\Pi k_i C_i e^{\Pi k_j C_j}}{\Pi k_i e^{\Pi k_j C_j}} + \text{other similar terms}$$

where the first term and the second term would
consist of rate constants $k_i, k_j$ etc. and the concen-
tration terms $C_i, C_j$ etc. But it appears from the
experimental results that only one of the terms is
more significant as compared to others. Hence, under
the circumstances, frequency would be given by

$$v = \frac{\Pi k_i}{\Pi k_j}$$

so that $v = \text{const.} \exp(-\Sigma E_i/RT)$

and hence $v = \text{const.} \exp(-\Sigma E_j/RT)$   \hspace{1cm} (3)

In Eq. (3), $\Sigma E_i$ and $\Sigma E_j$ denote the sum of energies
of activation of the reaction steps involved in the
product $\Pi k_i$ and $\Pi k_j$. It can be conceived that for
a set of reactions,

$$\Sigma E_i > \Sigma E_j$$

thus, justifying Eq. (1). The above analysis also
shows that $E$ would depend on the rate-determining
steps in the reaction sequence and hence need not
be the same for all Belousov-Zhabotinskii reactions
involving different organic substrates.

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for helpful correspondence.

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Faradic Effect of Direct Current, Alternating
Current & Pulsating Current: Current
Efficiency for the Conversion of Fe(III) into
Fe(II) & Vice Versa

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The nature and concentration of the electrolyte
wield a considerable influence in dc electrolysis.
Under similar conditions of electrolysis and at the
same concentration (i.e. 0.066N), the current efficiency
for conversion of Fe$^{3+}$ into Fe$^{2+}$ is 100% and for Fe$^{3+}$ into Fe$^{2+}$
it is 93.4%. On dilution of the electrolyte from 0.066
N to 0.033N, the current efficiency decreases by 25-35%.
On ac electrolysis the current efficiency is only 2.6%.
On electrolysis with ac superimposed on dc, the cur-
rent efficiency reduces by about 25% as compared to
that obtained with dc alone.

EXTENSIVE work has been done by Polit and
coworkers4 on on-Faradic electrolysis at low
concentration and low current density. At very
high dilution the conductance of the electrolyte is
expected to be very poor and to apply Faraday's
laws rigorously several other factors need be taken
into consideration. For industrial production it is
imperative that suitable conditions should be explored
so that the efficiency according to Faraday's
laws may be achieved up to 100%. Once this
ideal condition is achieved for a particular set of
experimental conditions, slight deviation from the
ideal condition by way of some physical properties
like current density, duration of time, change in
dilution, effect of superimposed current, etc. will
give us valuable information from the point of view
of operational conditions. In the present work
some easily reducible and oxidizable electrolytes
like ferric and ferrous salt solutions in 0.2N H$_2$SO$_4$
have been chosen for study as it would not only
avoid contamination of the electrode surfaces but
quantitative estimation of the oxidant or reductant
products would be more convenient.
The cell was so designed as to separate the catholyte from anolyte completely and at the same time ensuring uniform distribution of current density. The two coaxial cylinders, each of diameter 4 and 9-2 cm, were sealed at the bottom so as to serve as the two compartments for catholyte and anolyte. The cylinder with smaller diameter was joined in the upper half with an outlet tube carrying a small rose button sintered disc 1G4 (diam. 0-75 cm) so as to connect the electrolytes of the two compartments for achieving uniform distribution of current density. This device ensured complete separation of the catholyte from anolyte and prevented diffusion of either to a minimum. The Pt foil electrodes were washed with chromic acid, rinsed with ethanol and then heated to red heat to remove organic impurities, if any. The electrolytes in both the compartments were stirred with two separate mechanical stirrers of uniform speed.

In the series of cell circuit a silver voltmeter (whose silver bowl acted as a cathode and a thick silver foil acted as an anode) was used to find out the exact amount of current flowing through the experimental cell. A dc milliammeter and a standard rheostat were used in the cell circuit for controlling the magnitude of the current. Ac of frequency 50 Hz of known magnitude was superimposed on dc in series (pulsating current) and the reduction of Fe$^{3+}$ studied. Some of the observations were also made using ac at 50 Hz alone at two different current densities under similar conditions. The electrolysis with dc was carried out at different concentrations of the electrolyte, current densities and time interval, both for anodic and cathodic reactions.

The current efficiencies have been calculated on the basis of actual oxidation and reduction of the electrolyte as compared to the theoretical conversion expected considering the actual amount of current passed. All the reagents used were of AR grade and their solutions were made in doubly distilled water. The quantitative conversion of oxidant and reductant was estimated by titrating the electrolyte in the cell after each set of experiment, with dilute standard KMnO$_4$ solution using a microburette. The results obtained at varying current densities for different time periods at varying dilution of the electrolyte with dc, ac and superimposed current are given in Table 1.

For the same current density and time interval, the cathodic efficiency for the conversion of 0.066N Fe$^{3+}$ into Fe$^{2+}$ is 100% whereas the anodic efficiency for the reverse reaction (using same concentration) is 93-4% (Table 1). On further dilution of the electrolyte to 0.033N, the current efficiency for both reactions diminishes by 25-35%. The current efficiency also decreases at high current densities and with prolonged duration of electrolysis because of some side reactions and due to some time lag in quick removal of the resultant products from the electrode surface. The cathodic and anodic current efficiencies diminish by 2-5-3% in the electrolysis of equimolar mixtures of oxidant and reductant (Table 1), showing thereby that the presence of resultant product in the vicinity of electrode decreases the current efficiency appreciably.

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Conc.} & \text{Time min} & \text{Magnitude of current in milliamp} & \text{Cathodic efficiency} \% \\
\hline
N/15 & 30 & 10 & 93.4 \\
N/15 & 60 & 10 & 90.8 \\
N/30 & 30 & 10 & 87.8 \\
N/30 & 60 & 10 & 61.6 \\
N/15 & 30 & 20 & 53.4 \\
N/15 & 60 & 20 & 53.1 \\
N/15 & 30 & 10 & 100.0 \\
N/15 & 60 & 10 & 99.0 \\
N/30 & 30 & 20 & 96.3 \\
N/30 & 60 & 20 & 94.9 \\
N/15 & 30 & 20 & 62.9 \\
N/15 & 60 & 20 & 61.9 \\
N/15 & 30 & 10 & 96.7 \\
N/15 & 60 & 10 & 96.2 \\
N/15 & 30 & 20 & 93.8 \\
N/15 & 60 & 20 & 93.2 \\
\hline
\end{array}
\]

Table 1 — Electrolysis Using dc Alone

(Surface area of each electrode = 0.7 cm$^2$; temp. 25°±1°)

On carrying out ac electrolysis, the Fe$^{3+}$ is reduced to Fe$^{2+}$ and the current efficiency is only 2-6%. The current efficiency decreases with the increase in current density and duration of electrolysis$^{3-8}$ (Table 2).
NOTES

It is interesting to note that on carrying out electrolysis with ac (8.5 mA) superimposed on dc, the cathodic current efficiency (compared to the electrolysis by dc alone) decreases by 22% in spite of the fact that both ac and dc individually bring about the net reduction. On further increasing the magnitude of superimposed a.c. up to 40 mA, the current efficiency goes down by another 7% (Table 3). The decrease in current efficiency on superimposition of a.c. may not be disadvantageous to industrial production, as ac helps in the renewal of the electrode surfaces and which is itself a great advantage.

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References


Molecular Orbital Studies of Some Chromones

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π-Electronic structures of some γ-pyrone derivatives have been studied using the semi-empirical Pariser-Parr-Pople (PPP) method. Calculated π-electron densities and orbital energy values have been used quite successfully to discuss the 1H NMR chemical shifts and polarographic half-wave potentials.

The chemical and physical properties of compounds containing the γ-pyrone moiety have been studied in considerable detail. These systems are ideally suited to theoretical investigation and attempts have been made earlier to study their π-electronic structures. In our earlier theoretical work we have discussed the π-π* singlet-singlet transitions, the photoreactivity of C=C bond in the pyrone moiety and the orientational specificity of the photoaddition of 1,2-dimethoxyethylene to chromone.

In this note we make use of our calculated π-electron densities and orbital energies to discuss the available experimental proton NMR chemical shifts and polarographic half-wave potentials respectively.

The method of calculation and procedures for obtaining various integrals needed for the calculations are similar to those described earlier in our theoretical work.

It has been recognized for some time that proton chemical shifts (δH) in aromatic molecules can be correlated with the π-electron densities (qπ). Assuming the ring current contribution to remain constant for a series of chromones one would expect a linear relationship between δH and qπ on the carbon to which the proton is attached. A least squares fit analysis is carried out and a linear relation of form (1)

\[ \delta_H = 13.95(q_{\pi} - 1) - 7.31 \]

... (1)

is obtained for all the chromones studied in the present work. The correlation coefficient is found to be 0.88 indicating the fit to be fairly satisfactory. This type of linear relationship has been obtained earlier by many other workers in which they have studied different heterocycles and the proportionality constant in Eq. (1) has been estimated to be between 7 and 16 ppm/electron. Calculated electron densities and predicted proton chemical shifts are given in Table 1 along with available experimental data. Good agreement between the two can be seen.

Polarographic half-wave reduction potentials (E thước) are available for a series of chromones. A least squares fit analysis indicated a linear relation

Table I — PPP π-Electron Densities (qπ) AND 1H NMR Chemical Shifts (δH) IN SOME CHROMONES

<table>
<thead>
<tr>
<th>Position</th>
<th>(qπ - 1)</th>
<th>δH</th>
<th>Calc.</th>
<th>Obs. (a)</th>
</tr>
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<tr>
<td>CHROMONE</td>
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<tr>
<td>2</td>
<td>0.0517</td>
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<td>-7.88</td>
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<tr>
<td>3</td>
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<td>5</td>
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<td></td>
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<tr>
<td>6</td>
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<tr>
<td>7</td>
<td>0.0265</td>
<td>-7.68</td>
<td>-7.58</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.0329</td>
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<tr>
<td>5-OH-CHROMONE</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
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<tr>
<td>3</td>
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<td></td>
</tr>
<tr>
<td>2-Me-CHROMONE</td>
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<td>8</td>
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<td>-6.84</td>
<td>-7.36</td>
<td></td>
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</table>

(a) Obtained from ref. 7.