

Arrhenius plots for the reaction of butyl vinyl ether with excess of CBrCl_3 :

1) $\log V_{st}/[\text{BVE}]$; 2) $\log k_2/k_4$.

TABLE 2. Addition of CBrCl_3 to phenyl vinyl ether in excess of the former at 25° .

[PVE], M	Steady-state rate V_{st} , determined		V_{st} , [PVE], s^{-1}	V_e V_{st}	$\Delta\Delta M_e$, divisions	k_2/k_4
	dilatometrically, $\text{M}^{\text{th}} \text{s}^{-1}$	from adiabatic temp. rise, divisions s^{-1}				
0.90	$6.55 \cdot 10^{-8}$	—	$7.3 \cdot 10^{-8}$	—	—	—
0.61	3.85	6.9	6.3	0.034	56	$1.9 \cdot 10^{-4}$
0.30	1.9	3.4	6.4	0.053	22	1.75
0.30	2.2	6.6	7.3	0.059	48	2.3

this concentration range were used to calculate the constant k_2/k_4 from Eqn. (4). The diagram shows Arrhenius plots for the quantities $k_2/k_4^{1/2}$ and $V_{st}/[\text{BVE}]$, the latter quantity being proportional to the former. The fact that these straight lines are parallel shows that the activation energy of reaction (3) is close to zero. For reaction (2) the activation energy determined from the slope of the straight line for $V_{st}/[\text{BVE}]$ is $7.7 \text{ kcal mole}^{-1}$. Thus $k_2/k_4 = 316 \exp(-7700/RT)$. If we take for k_4 the previous value¹ of $10^8 \text{ litre mole}^{-1} \text{ s}^{-1}$, we obtain $k_2 = 3.16 \times 10^{10} \exp(-7700/RT)$.

Reaction of Bromotrichloromethane with Phenyl Vinyl Ether†

The relative contraction for this reaction is $26.6 \text{ cm}^3 \times \text{mole}^{-1}$. The reaction was studied at 25° . It is of the first order over the concentration range 0.30–0.90 M with respect of the phenyl vinyl ether. No dark reaction is present. The experimental results are collected together in Table 2. The average value of k_2/k_4 is 2.0×10^{-4} (at 25°). Taking k_4 as 10^8 , we obtain $k_2 = 2.0 \times 10^4 \text{ litre mole}^{-1} \text{ s}^{-1}$.

† Phenyl vinyl ether was prepared in the laboratory of Professor M. F. Shostakovskii and used without further purification.

The values obtained for the constants k_2 at 25° — of 2.0×10^4 for phenyl vinyl ether, and 7.8×10^4 for butyl vinyl ether — differ little from the value of 1.8×10^4 found for hept-1-ene in the previous paper.

SUMMARY

In addition reactions of the CCl_3 radical to vinyl ethers, no appreciable polar effect is developed.

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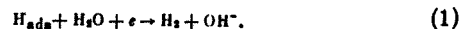
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BEHAVIOUR OF ATOMIC HYDROGEN ON A PURE IRON SURFACE

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We have previously^{1,2} investigated the mechanism of the hydrogen overpotential on Armco iron in dilute acid and alkali by determining the dependence of the overpotential at constant cathodic polarisation on the surface concentration of atomic hydrogen. Measurements were made on an iron diaphragm electrode. The concentration of atomic hydrogen was increased by supplying it by diffusion to what we termed the "diffusion" side of the diaphragm from the opposite, "polarisation" side. The latter was cathodically polarised in alkali solutions containing HgO or in dilute acids containing $\text{Pb}(\text{NO}_3)_2$.² It was found that in alkali² the atomic hydrogen increases η at low cathodic polarisations and lowers it at high polarisations. According to the theoretical ideas developed by Frumkin³, an increase in η under the influence of additional quantities of atomic hydrogen indicates that its removal by recombination or electrochemical desorption is slow compared with the discharge stage on a clean surface, while a decrease indicates rapid removal by electrochemical desorption



In dilute acid we were unable¹ to detect any effect of atomic hydrogen on the hydrogen overpotential of Armco iron. This insensitivity of η to additional quantities of atomic hydrogen in dilute acids could be explained either by its rapid removal by recombination or by poor wetting of the electrode surface by the acid, as a result of which the

atomic hydrogen arriving by diffusion recombines in pores and cracks which are not wetted by the acids, and thus does not enter the region where the electrode reaction is taking place.

It was of considerable interest to see whether the phenomena observed on Armco iron occur on zone-melted iron (impurity content below 0.01%)†. Measurements were made by the previous method^{1,2} in an apparatus similar to that used for measurements on a palladium diaphragm electrode⁴. In this apparatus airtightness between a plane-parallel ground-glass joint and the diaphragm was achieved by tightly clamping the polarisation and diffusion cells. The outside of the ground-glass joint was sealed with pure paraffin wax to diminish diffusion of atmospheric oxygen into the solution through the gap between the diaphragm and the plane-parallel joint. The dilute acid was prepared from twice distilled H_2SO_4 , and the alkali by decomposing sodium amalgam. Before an experiment the solutions used were purified by cathodic polarisation at 10^{-2} A cm^{-2} on electrodes of the same type of iron in an ancillary cell⁴.

In 1 N NaOH the zone-melted iron showed the same variation in η under the influence of additional quantities of atomic hydrogen as did Armco iron: at $\eta < 0.35$ V, atomic hydrogen increases η ; but at $\eta > 0.35$ V, it lowers the latter. The absolute variation in η was of the same order of magnitude as on Armco iron.

On zone-melted iron in 1 N H_2SO_4 , atomic hydrogen lowered η over the whole range of polarisations investigated (Fig. 1). Hence under these conditions atomic hydrogen is removed by electrochemical desorption, the rate of this stage exceeding that of the discharge stage $H^+ + e \rightarrow H_{ads}$. Similar results for zone-melted iron have been obtained by Bockris and Drazic⁵. These workers also showed, by determining decay curves, that the capacitance on zone-melted iron in 0.4 N H_2SO_4 is one-quarter of that on iron containing up to 0.2% of impurities, and the surface coverage with adsorbed hydrogen does not exceed one-tenth of a monolayer on the zone-melted iron. Hence it is probable

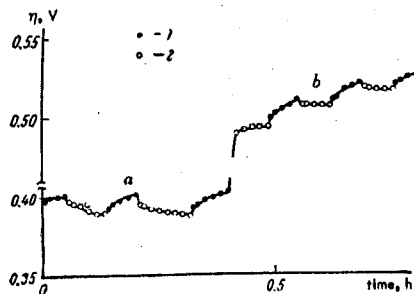


Fig. 1. Effect of diffusing hydrogen on overpotential at zone-melted iron in 1 N H_2SO_4 at current densities ($mA\ cm^{-2}$): a) 1.6; 1) $i' = 0$; 2) $i' = 2.4$; b) 8; 1) $i' = 0$; 2) $i' = 2$.

that the energy of the $M-H_{ads}$ bond is lower on this kind of iron than on more impure iron, and the rate of removal of adsorbed hydrogen by electrochemical desorption should be greater. This perhaps explains why we have been able to observe on zone-melted iron a decrease in hydrogen overpotential in the presence of additional quantities of atomic hydrogen.

We have repeated on zone-melted iron poisoned with mercury the experiments to determine the ratio $\Delta i/i'$ ^{6,7} in 1 N NaOH (Δi being the increase in current in the presence of the diffusing hydrogen at constant η , and i' the quantity of hydrogen diffusion in 1 s expressed in electrical units). It would appear from its physical meaning that the ratio $\Delta i/i'$, which indicates the number of water molecules whose discharge by electrochemical desorption is facilitated by each hydrogen atom which has arrived by diffusion, cannot exceed unity. In the measurements^{6,7} on Armco iron poisoned with mercury, however, $\Delta i/i'$ was always about 2. This result is incomprehensible, and we considered it desirable to verify it on zone-melted iron. Measurements carried out as in Ref. 7 have shown that on zone-melted iron, too, the ratio $\Delta i/i'$ also exceeds unity and is about 2.

In our above experiments the effect of the concentration of atomic hydrogen on the kinetics of cathodic hydrogen evolution was determined while atomic hydrogen was fed to the electrode surface, and the total quantity of molecular hydrogen removed from the latter exceeded the amount equivalent to the current through the electrode. On mercury-poisoned zone-melted iron in alkali solution, we have also determined the variation in the kinetics of cathodic hydrogen evolution when the quantity of hydrogen recombining to form molecules on the electrode surface is relatively smaller than the current. In this case part of the atomic hydrogen is removed by diffusion, from the electrode surface under examination, into the metal towards the opposite side of the diaphragm. In these experiments the side A, to which the hydrogen diffused, was in contact with the alkali solution in air, and was not at first subjected to polarisation. Its surface was strongly oxidised. The opposite side B of the diaphragm, which constituted the test electrode, was strongly poisoned with mercury, and was cathodically polarised with a current of $i_B = 6\ mA\ cm^{-2}$ in 1 N NaOH. The quantity of hydrogen evolved on side B corresponded to the current through the electrode. When cathodic polarisation was applied to the side A, its surface was reduced, and hydrogen began to diffuse from surface B. The amount of hydrogen evolved on B decreased below the quantity equivalent to the current, and the electrode potential became more negative (η_B increased) at constant i_B . Subsequent termination of the cathodic polarisation of side A resulted in slow oxidation of it by atmospheric oxygen, the diffusion of hydrogen diminished, and η_B gradually fell. These measurements are plotted in Fig. 2.

These results have also been used to calculate $\Delta i_B/i'$ by determining, from the deviation from Faraday's law of the quantity of hydrogen evolved on B during its cathodic polarisation with a current $i_{B,1}$, the diffusion of hydrogen i' from the surface B, together with the change in overpotential $\Delta\eta_B$. After this the current $i_{B,2}$, corresponding to $\eta_{B,2} = \eta_{B,1} + \Delta\eta_B$, was measured in the absence of diffusion of hydrogen from surface B, and the quantity $\Delta i_B = i_{B,2} - i_{B,1}$ was calculated; this showed how much more rapidly cathodic hydrogen evolution could occur on B at $\eta_{B,2}$ if all the discharged hydrogen recombined on it instead of part diffusing to the opposite side. The value of $\Delta i_B/i'$ obtained in this way was also greater than unity, about 1.9.

† The zone-melted iron was kindly supplied to A. N. Frumkin by Professor H. H. Uhlig of the Massachusetts Institute of Technology, to whom we express our thanks.

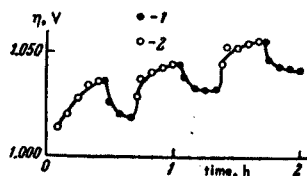


Fig.2. Variation in overpotential on zone-melted iron poisoned with mercury in 1 N NaOH as a function of the quantity of hydrogen v_{H_2} (in mA cm^{-2}) which recombines on its surface during cathodic polarisation with a current of 6 mA cm^{-2} : 1) 6; 2) 5.9.

Such a high value of $\Delta i/i'$ could be explained by variation in the surface coverage of an electrode with adsorbed hydrogen (produced by supplying or removing atomic hydrogen) being accompanied by a change in the energy characteristics of the surface owing to a change in the degree of poisoning with mercury, since such poisoning lowers the surface concentration of adsorbed hydrogen. A mercury-poisoned iron surface contains fine droplets of mercury, which can act as donors or acceptors of mercury atoms as adsorption of the latter increases or decreases respectively. In this case the measured acceleration of the cathodic evolution of hydrogen with increase in its surface concentration will be too high, since such acceleration is caused by two factors — electrochemical desorption and increase in the rate of discharge of water molecules on the unoccupied portions of the surface as a result of its diminished poisoning with mercury.

Some confirmation of a change in degree of poisoning of iron with mercury in the presence of diffusing hydrogen is provided by our observations⁷ on the partial irreversibility of the decrease in η on mercury-poisoned iron after diffusion of hydrogen has ceased, when η was always rather lower than before it had started. This argument may concern the magnitude of the decrease in overpotential produced by diffusing hydrogen, but casts no doubt on the reality of the main effect, which is proved by the observed decrease in η on unpoisoned iron in alkali² and acid, and also by the influence of the structure of the double layer on the decrease in η .⁸

The correctness of the proposed explanation of the ratio $\Delta i/i'$ exceeding unity cannot be regarded as established unequivocally. In fact, if the observed decrease in η on mercury-poisoned iron in the presence of diffusing hydrogen were caused by a change in the degree of poisoning with mercury, the ratio $\Delta i/i'$ could fluctuate within wide limits, whereas in the large number of experiments which we have carried out it was always about 2. Therefore the observed value of $\Delta i/i' \approx 2$ is, perhaps, not determined by extraneous factors, but reflects some as yet unknown peculiarities in the mechanism of electrochemical desorption.

We express our gratitude to Academician A. N. Frumkin for valuable advice and discussions.

SUMMARY

1. On zone-melted iron (99.99% pure) in dilute acid, atomic hydrogen is removed rapidly by electrochemical desorption, and the overpotential is determined by the discharge stage.
2. In dilute alkali the relations between the rates of the various stages in the cathodic evolution of hydrogen are the same on zone-melted iron as on Armco iron.

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SELF-DIFFUSION IN A LIQUID

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Let us start from the postulate that the motion of atoms in a liquid consists of an oscillation about temporary positions of equilibrium. During time τ the centres of equilibrium of a large group of particles do not change their positions. Hence during this time τ the system is located in a certain part of the phase space, and the distribution of phase points in the phase space can be described by a conditional distribution function normalised in the volume ΔV_T

$$f^{NN}(\vec{p}_1, \vec{r}_1 / \vec{r}_1^0) = \frac{f^N(\vec{p}_1, \vec{r}_1)}{\int \dots \int \int \dots \int \Delta_N f^N(\vec{p}_1, \vec{r}_1) d\vec{p}_1 d\vec{r}_1} \quad (1)$$

At the end of the time interval τ at least one equilibrium centre "jumps" to a different position, and the phase point enters a different region of ΔV_T . This region corresponds to a new conditional equilibrium function. During times $t \gg \tau$, i.e. over a macroscopically large time interval, all possible configurations of the equilibrium centres are realised, and the phase point traverses the whole of the phase volume. If we denote by $(1/V^N)\varphi^N(\vec{r}_1^0)$ the probability density that a specified configuration $\{\vec{r}_1^0\}$ of the equilibrium centres will be achieved, we have for the conditional distribution function of any order

$$f^{(nn)}(\vec{p}_1, \vec{r}_1 / \vec{r}_1^0) = \frac{1}{V^{N-n}} \int \dots \int \varphi^{(N-n)} d\vec{r}_1^0 \int \dots \int \Delta_{(N-n)}^N d\vec{r}_1 \quad (2)$$