

rate of movement of the zone enables the impurity content to be decreased by factors of 8-9, the purity of n-octane being raised from 91.6 to 99.05 mole %, and that of n-hexane from 97.4 to 99.7 mole %.

In this work it was not our aim to obtain materials of maximum purity, but to work out a more or less simple technique enabling zone melting to be undertaken at low temperatures. By increasing the number of passes to ten, working with purer starting materials than in the present case, and perhaps using a slower rate of movement of the zone, it is possible to effect considerable purification by this method, and obtain substances having a high degree of purity.

SUMMARY

1. A method has been worked out for purifying organic substances which crystallise at low temperatures by zone melting in a gastight vessel, out of contact with air.
2. The zone melting of n-octane ($t_{\text{cryst}} -56.8^\circ$) and of n-hexane (-95.3°) has been carried out. After five passes the impurity content has decreased by factors of 8-9.

one adsorbed hydrogen atom³; it was found to be 0.2-0.4 m² (with an apparent surface of 2 cm²). The concentration of C₂H₅OH and CH₃CHO was 0.5 M in all the experiments reported. Potentials (φ) are given relative to that of a reversible hydrogen electrode in the same solution.

The charging curves obtained in 0.1 N H₂SO₄ after washing ethanol and acetaldehyde from the electrode (Figs. 1 and 2, curves 1) show clearly marked plateaux, representing the oxidation of firmly adsorbed layers of C₂H₅OH and

1. A.G. Anikin, G.M. Dugacheva, V.M. Presnyakova, and S.P. Bykova, Zhur. Fiz. Khim., **36**, 2074 (1962) [Russ. J. Phys. Chem., **1115** (1962)].
2. H. Schildknecht and A. Mannl, Angew. Chem., **69**, 634 (1957).
3. J.S. Ball, R.V. Helm, and C.R. Ferrin, Petrol. Engr., **30**, 36 (1958).
4. P. Süe, J. Pauly, and A. Nonaille, Bull. Soc. chim. France, No. 5, 593 (1958).
5. H. Röck, Naturwiss., **43**, 81 (1956).
6. W.G. Pfann, "Zone Melting" (Translated into Russian), Metallurgizdat, Moscow, 1960.
7. F.D. Rossini, B.J. Mair, and A.J. Streiff, "Hydrocarbons from Petroleum", Reinhold, New York, 1953.
8. A.G. Anikin and G.M. Dugacheva, Dokl. Akad. Nauk SSSR, **119**, 939 (1958).

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CHEMISORPTION OF ETHANOL AND ACETALDEHYDE ON PLATINUM AND INFLUENCE OF ANIONS OF SUPPORTING ELECTROLYTE

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The technique which we have employed to investigate the adsorption of ethanol and acetaldehyde on platinised platinum¹ is based on anodic oxidation in the adsorbed layer^{2,3}. The organic compound was introduced at the potentials of the electrical double layer (about 500 mV). The true surface of the electrode was calculated from the length of the hydrogen arrest on the charging curve in 0.1 N H₂SO₄, on the assumption that 1 cm² of surface contained 1.31×10^{15} platinum atoms⁴ and that, at a potential of -0.01 V in 0.1 N H₂SO₄, one surface platinum atom is associated with

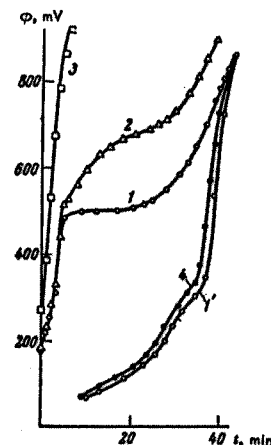


Fig. 1. Charging curves (at current density 10^{-4} A cm⁻² based on apparent surface) in the presence of ethanol adsorbed on the surface of platinum in solutions of: 1) 0.1 N H₂SO₄; 1') as above, reverse curve; 2) 0.1 N HCl; 3) 0.09 N KBr + 0.01 N HCl; 4) reverse charging curve in pure 0.1 N HCl.

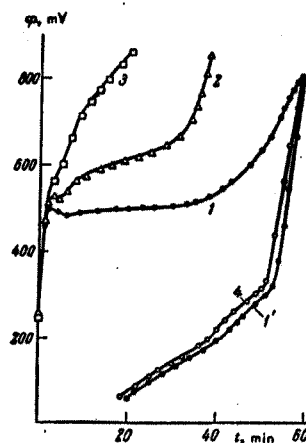


Fig. 2. Charging curves (at current density 10^{-4} A cm⁻² based on apparent surface) in the presence of acetaldehyde adsorbed on the surface of platinum in solutions of: 1) 0.1 N H₂SO₄; 1') as above, reverse curve; 2) 0.1 N HCl; 3) 0.09 N KBr + 0.01 N HCl; 4) reverse charging curve in pure 0.1 N HCl.

CH_3CHO on the platinum surface. The facts that after eight rinsings considerable amounts of these substances remained on the electrode surface, and that further increase in the number of washes had practically no effect on the size of the arrests on the charging curves for $\text{Pt}(\text{X})_{\text{ads}}$, show that chemisorption of $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO , not physical adsorption, has taken place on the platinum surface. In the case of ethanol, this conclusion is supported also by the absence of adsorbed alcohol from the electrode surface when it is added at the reversible hydrogen potential and the electrode is subsequently washed: the charging curve after washing is identical with that in pure $0.1\text{ N H}_2\text{SO}_4$. If, however, after the electrode potential has become steady (it undergoes a negative change to $155 \pm 5\text{ mV}$ when $\text{C}_2\text{H}_5\text{OH}$ is introduced at 500 mV), hydrogen is passed through the solution, the potential rapidly drops to zero. The charging curve after the electrode has been washed shows that hydrogen desorbs only about half of the ethanol, this proportion being practically independent of the duration of the stream of hydrogen after the reversible hydrogen potential has been established. Thus previously adsorbed hydrogen prevents the adsorption of ethanol, and conversely. Analogous phenomena are observed in the simultaneous adsorption of oxygen and anions on platinum⁶. It is not excluded that chemisorption of $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO is accompanied by complete breakdown of the original molecules, and that dehydrogenation products (perhaps chemisorbed radicals) are present on the electrode.

Since the true surface of platinised platinum contracts somewhat with time, the adsorption of an organic substance X was characterised by the ratio of the length of the plateau on the charging curve of $\text{Pt}(\text{X})_{\text{ads}}$ † to the length of the hydrogen arrest on the charging curve in pure $0.1\text{ N H}_2\text{SO}_4$ ‡ determined on the same day. This quantity remains constant within the limits of experimental error and the accuracy of graphical calculation, and has the respective values

$$i_{\text{H}_2\text{SO}_4}^{\text{C}_2\text{H}_5\text{OH}} = 1.2 (\pm 0.1); i_{\text{H}_2\text{SO}_4}^{\text{CH}_3\text{CHO}} = 1.4 (\pm 0.1).$$

The charging curves for ethanol and acetaldehyde adsorbed on platinum indicate that, within the potential range of the double layer, they are oxidised at practically the same rate (same potential of plateaux at the same current density). The good agreement between the cathodic portions of these charging curves (Figs. 1 and 2, curves 1') and the reverse charging curve in $0.1\text{ N H}_2\text{SO}_4$ (curves 4) indicates that the oxidation products do not include any considerable quantities of substances which affect the ability of platinum to adsorb hydrogen. This shows that the oxidation of adsorbed ethanol yields no appreciable amount of acetaldehyde. Adsorbed ethanol and acetaldehyde are most probably oxidised to acetic acid, since this is oxidised only very slowly in the potential range of the double layer^{7,8}.

† It was assumed that $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO were practically completely oxidised up to 750 mV , since the potential range $720\text{--}780\text{ mV}$ contains the steepest portion of the charging curve of $\text{Pt}(\text{X})_{\text{ads}}$, and when the polarisation is switched over to cathodic in this potential range, curves are obtained which coincide well with the reverse charging curve in $0.1\text{ N H}_2\text{SO}_4$.

‡ In order to calculate the latter, the initial portion of the charging curve and the linear portion of the double-layer region were extrapolated to -0.01 V .

§ The oxidation of acetic acid at potentials below the start of oxygen evolution is confirmed by the considerable hysteresis of the charging curve in $0.1\text{ N H}_2\text{SO}_4 + 0.5\text{ M CH}_3\text{COOH}$ and the drop in potential (to $280\text{--}260\text{ mV}$) when acetic acid is added to $0.1\text{ N H}_2\text{SO}_4$.

The high value of $i_{\text{CH}_3\text{CHO}}$ is perhaps due to polymerisation of the acetaldehyde⁹.

In the presence of the Cl^- anion the plateau representing oxidation of the chemisorbed organic compound becomes shorter (Figs. 1 and 2, curves 2). In the presence of Br^- , however, the plateau disappears altogether with $\text{C}_2\text{H}_5\text{OH}$, and is converted into a slight arrest at $800\text{--}580\text{ mV}$ [sic. (Ed. of Translation)] with CH_3CHO curves 3). Thus, depending on the anion of the supporting electrolyte, the adsorption of $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO diminishes in the sequence $\text{SO}_4^{2-} > \text{Cl}^- > \text{Br}^-$, which is obviously associated with specific adsorption of the halide ions, tending to inhibit chemisorption of the organic compound.

The tendency of halide anions to suppress the oxidation of ethanol has been established in several papers^{10,11}, but the diminished surface concentration of chemisorbed $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO in the presence of Cl^- and Br^- (compared with SO_4^{2-}) has probably been established for the first time in the present investigation.

The oxidation of adsorbed ethanol and acetaldehyde at higher potentials in 0.1 N HCl than in $0.1\text{ N H}_2\text{SO}_4$ shows that, in addition to lowering the surface concentration, the presence of Cl^- ions also increases the overpotential accompanying oxidation of these compounds. In the presence of Br^- no chemisorption of $\text{C}_2\text{H}_5\text{OH}$ is observed at all, while the adsorption of CH_3CHO is slight and the adsorbed aldehyde is removed at still higher potentials than in the presence of Cl^- .

The positive shift in potential when the electrode is washed (Fig. 3) is obviously due to removal of the less firmly held portions of the organic compound from the electrode surface†. With both ethanol and acetaldehyde the change in potential decreases in the sequence $\text{SO}_4^{2-} > \text{Cl}^- > \text{Br}^-$, which is the sequence of decreasing adsorption of $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO .

Since halide anions tend to inhibit the oxidation of ethanol and acetaldehyde, it could be expected that the rate and extent of change in the potential produced by addition of these substances would decrease according to the anion of the supporting electrolyte in the sequence $\text{SO}_4^{2-} > \text{Cl}^- > \text{Br}^-$, which is what we see in Fig. 4. This effect is especially strongly developed in the case of ethanol in the presence of Br^- : in this case the electrode potential reaches values corresponding to the start of hydrogen evolution after only 40 min , and then continues to become slowly more negative.

The absence of a hydrogen arrest on the charging curve of $\text{Pt}(\text{CH}_3\text{CHO})_{\text{ads}}$ (Fig. 2, curves 1 and 2) and the initial surge of the potential to more negative values than the steady potential finally reached when acetaldehyde is added to $0.1\text{ N H}_2\text{SO}_4$ and 0.1 N HCl (Fig. 4, curves 1' and 2') show that the nature and mechanism of the establishment of potential in acetaldehyde solutions differ somewhat from those in the case of ethanol¹. In seeking the causes of these differences, account must probably be taken of two

¶ Polymerisation of acetaldehyde may, perhaps, explain the fact that slight additional energy is required to start oxidation [slight maximum before the beginning of the plateau on the charging curve of $\text{Pt}(\text{CH}_3\text{CHO})_{\text{ads}}$ in $0.1\text{ N H}_2\text{SO}_4$ and 0.1 N HCl].

† It must be assumed here that formation of the potential-determining species (in the case of $\text{C}_2\text{H}_5\text{OH}$, probably H_{ads} ¹) from the adsorbed molecule of the original organic compound is at least partly reversible.

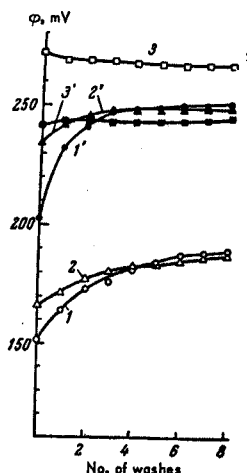


Fig. 3. Variation in potential of platinum electrode during the washing off of ethanol and acetaldehyde (the latter denoted by a prime ') in: 1) 0.1 N H_2SO_4 ; 2) 0.1 N HCl ; 3) 0.09 N KBr + 0.01 N HCl .

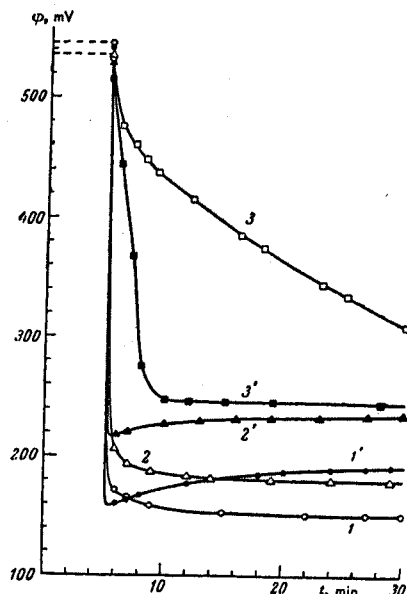


Fig. 4. Curves showing change in potential accompanying addition of ethanol and of acetaldehyde (denoted by a prime ') to: 1) 0.1 N H_2SO_4 ; 2) 0.1 N HCl ; 3) 0.09 N KBr + 0.01 N HCl .

characteristic features of CH_3CHO — its tendency not only to oxidation but also to hydrogenation on the surface of platinum¹² and its tendency to polymerisation†.

In phosphate buffer solutions§ increase in pH was accompanied by a decrease in the amount of ethanol adsorbed and an increase in the overpotential involved in its oxidation. At a current density of 10^{-4} A cm^{-2} (based on the apparent surface) oxidation of adsorbed ethanol begins in 0.1 N H_2SO_4 (pH 1.26) at 505 mV and in phosphate buffers (pH 5.3, 8.00, and 11.0) at 545, 547, and 710 mV respectively. These results cannot be explained by the influence of the pH, since firstly the oxidation potential of the adsorbed alcohol does not increase uniformly with increase in pH, and secondly the oxidation of chemisorbed ethanol takes place at practically the same potential in 0.1 N KOH (pH 13) as in 0.1 N H_2SO_4 . Thus the observed effects are obviously due to inhibition of the chemisorption and oxidation of adsorbed ethanol by the anions of phosphoric acid, whose action follows the sequence $(\text{SO}_4^{2-}) < \text{H}_2\text{PO}_4^- < \text{HPO}_4^{2-} < \text{PO}_4^{3-}$. The quantity of ethanol adsorbed in 0.1 N KOH constitutes about one-fifth of the amount in 0.1 N H_2SO_4 , which may be due either to its removal by chemical reaction with the alkali during washing¹³ or to the desorbing action of the OH^- anion.

We express our profound gratitude to Academician A. N. Frumkin for many discussions and for his interest in the work.

SUMMARY

1. After $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO have been rinsed off an electrode, the charging curves show arrests corresponding to the oxidation of films of these substances chemisorbed on the platinised platinum surface.
2. The presence of the anions Cl^- and Br^- produces a decrease in surface concentration and an increase in the overpotential accompanying oxidation of chemisorbed $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO .
3. The anions of phosphoric acid also tend to inhibit chemisorption of $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO , as well as oxidation of the chemisorbed compounds, the effect increasing in the sequence $(\text{SO}_4^{2-}) < \text{H}_2\text{PO}_4^- < \text{HPO}_4^{2-} < \text{PO}_4^{3-}$.

1. A. N. Frumkin and B. I. Podlovchenko, Dokl. Akad. Nauk SSSR, **150**, 349 (1963); B. I. Podlovchenko, O. A. Petril, and A. N. Frumkin, *ibid.*, **153**, 379 (1963).
2. A. I. Shlygin, "Trudy Soveshchaniya po Elektrokhemii" (Proceedings of the Conference on Electrochemistry), Izd. Akad. Nauk SSSR, 1953, p. 322.
3. T. O. Pavela, Ann. Acad. Sci. Fennicae, Ser. AII, No. 59 (1954).
4. A. N. Frumkin and A. I. Shlygin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, No. 5, 773 (1936).
5. M. Breiter, H. Kammermaier, and C. A. Knorr, Z. Elektrochem., **60**, 37 (1956).
6. V. E. Kazarinov and N. A. Balashova, Dokl. Akad. Nauk SSSR, **139**, 641 (1961).

† It has now been established that $\text{C}_2\text{H}_5\text{OH}$ is also hydrogenated by adsorbed hydrogen, but with considerably greater difficulty than is CH_3CHO .

§ The phosphate buffers were prepared by neutralising 0.3 N KH_2PO_4 with 0.3 N KOH .

7. Yu. V. Vasil'ev, Thesis, Moscow, 1962.
8. W. D. Harkins, Chem. Rev., **29**, 385 (1941).
9. M. Breiter and S. Gilman, J. Electrochem. Soc., **109**, 622 (1962).
10. V. N. Modestova, Thesis, Moscow, 1952.
11. E. A. Aikazyan and Yu. V. Pleskov, Zhur. Fiz. Khim., **31**, 205 (1957).
12. D. V. Sokol'skii and T. M. Beloslyudova, Dokl. Akad. Nauk SSSR, **145**, 834 (1962).
13. P. Ballinger and F. A. Long, J. Amer. Chem. Soc., **82**, 795 (1960).

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DETERMINATION OF ABSOLUTE RATE CONSTANTS OF RADICAL REACTIONS. II. ADDITION OF BROMOTRICHLO- METHANE TO BUTYL VINYL AND PHENYL VINYL ETHERS

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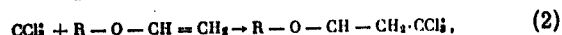
The previous paper¹ has described a method for measuring absolute rate constants for elementary reactions from the adiabatic rise in temperature in the non-stationary stage of a chain process. The addition of CBrCl₃ to cyclohexene and to heptene was investigated. Comparison of the results with published data showed that the rate constants for addition of the CCl₃ radical increase in the sequence cyclohexene < vinyl acetate < hept-1-ene < anthracene < styrene, and differ little in absolute magnitude from the corresponding constants for the CH₃ radical. Velocity constants for addition of the CF₃ radical are 2-4 orders of magnitude higher, which must be regarded as due to a polar effect². In the above reactions of the CCl₃ radical the polar effect is obviously weakly developed.

In the present work the rate constants have been determined for the addition of CBrCl₃ to butyl vinyl ether (BVE) and to phenyl vinyl ether (PVE). The presence of the electron-donor oxygen atom close to the double bond could be supposed to reveal a polar effect with the CCl₃ radical as well.

Examination of the kinetics of chain reactions of this type in the presence of a large excess of one of the components, for example CBrCl₃, yields for the steady-state reaction velocity the expression

$$V_{st} = I^{1/2} \frac{k_2}{k_4^{1/2}} [E], \quad (1)$$

where I is the rate of initiation, $[E]$ is the concentration of the ether, and k_2 and k_4 are rate constants of the reactions



After illumination, a further quantity $\Delta\Delta M$ of reaction product is formed, which is linked¹ with the constants k_2 and k_4 by the equation

$$\Delta\Delta M = -\frac{k_2}{k_4} [E] \ln(1-q), \quad (4)$$

where $q = (V_{st} - V_0)/(V_{st} + V_0)$, in which V_0 is the "background" rate of the reaction, not recorded by the adiabatic temperature rise method. The background velocity is produced by either weak photochemical or spontaneous thermal initiation.

Reaction of Bromotrichloromethane with Butyl Vinyl Ether

Butyl vinyl ether was dried over metallic sodium at 50°, distilled at 100 mmHg, and recondensed in a high vacuum into ampoules, which were sealed and stored in a refrigerator; $n_D^{20} = 1.4010$. The relative contraction for the reaction of CBrCl₃ with butyl vinyl ether, determined from the kinetics of compression³, is 19.3 cm³ mole⁻¹, which is close to the value obtained from the density of the addition product⁴. A dark reaction, which served as background reaction, was observed at concentrations of the ether of 0.3 M and above. At lower concentrations, the background rate was produced by using a screen which greatly weakened the light, as described previously¹. The quantity $\Delta\Delta M$ is measured directly in divisions of the scale on the paper strip of the recording instrument. In order to express this quantity as a molarity, the steady-state rates of photochemical and dark reactions were determined dilatometrically, and the difference between them was compared with the rate of movement of the recording pen (in divisions s⁻¹) under the same steady-state conditions. Measurements were made with different sensitivities of the recording instrument depending on the magnitude of the effect. Table 1 gives experimental results obtained in the presence of excess of CBrCl₃.

As is evident from Table 1, a reaction of the first order with respect to the ether occurs only when the concentration of the latter does not exceed 0.3 M†. Results obtained in

TABLE 1. Addition of CBrCl₃ to butyl vinyl ether in excess of the former.

Temp., °C	[BVE], M	Steady-state rate V_{st} , determined		V_{st} , s ⁻¹ [BVE]	V_0 V_{st}	$\Delta\Delta M$, divisions	k_2/k_4
		dilatometrically, M s ⁻¹	from adiabatic temp. rise, divisions s ⁻¹				
15	0.77	15.0·10 ⁻⁴	6.7	1.95·10 ⁻⁴	0.063	54	—
15	0.30	3.81	6.9	1.27	0.12	42	5.6·10 ⁻⁴
15	0.28	3.41	6.0	1.22	0.090	39	4.6
25	0.57	3.70	6.2	2.4	0.059	57	—
25	0.29	5.87	3.1	2.02	0.057	30	8.2
25	0.14	2.60	3.5	1.86	0.11	19	7.1
25	0.068	1.30	2.0	1.91	0.18	10	7.5
40	0.25	9.18	4.4	3.67	0.096	39	15.3

† Strictly speaking, Eqn. (1) is not applicable in the presence of a dark reaction. It can easily be shown that making allowance for the latter results in the appearance of the factor $(1 - V_0^2/V_{st}^2)^{1/2}$ on the right-hand side of this equation. Since V_0/V_{st} did not exceed 0.2 in our experiments, this factor differs very little from unity. Therefore Eqn. (1) can be applied without any correction.