the reversed air/ethylene flame are available. These establish the presence of carbonyl and associated hydroxyl groups. There is also strong absorption in the regions 700–900 cm.$^{-1}$ and 2,800–3,100 cm.$^{-1}$. Similar absorption is also exhibited by the soluble material from the various flames burning at reduced pressure. The ultra-violet absorption spectra from the deposits collected from normal flames of methane, ethylene and propane burning under reduced pressure all show very similar characteristics. Decreasing absorption between 2200 A. and 4000 A. was exhibited with small, variably spaced maxima, some of which occurred at 2875, 3000, 3350 and 3750 A.

A more detailed account of these investigations is to be published elsewhere.

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Calculation of Surface Areas from Room-Temperature Adsorption Isotherms

ADSORPTION studies currently in progress in these laboratories are providing evidence that the application of the Brunauer–Emmett–Teller method to room-temperature isotherms is in certain instances liable to lead to substantial errors. The adsorption of methanol on lignites at 25° C. presents a case in point.

The isotherms are here generally of the type recently described by Jura and Powell[1], that is, the rate of adsorption falls rapidly to a negligible value as monolayer capacity is approached, and subsequent adsorption (probably largely governed by swelling of the adsorbent) proceeds at a relatively fast and constant rate. Monolayer capacities can therefore be calculated directly either from the point of intersection of the two (slightly extrapolated) isotherm branches[2], or alternatively, as Jura and Powell have done, from the point at which the initial rate of adsorption has fallen to zero. The two methods are formally identical. In either case, however, it turns out that whereas the value of s_0 thus obtained is in very good agreement with that derived from, for example, Gregg's FA–$F\Sigma$ plot[3], it is up to 50 per cent higher than the figure computed from the Brunauer–Emmett–Teller graph. The results set out in the accompanying table, in which Σ_1 refers to the Brunauer–Emmett–Teller values and Σ_2 to surface areas calculated from the point of intersection of the isotherm branches, illustrate this; in all cases, the cross-sectional area per methanol admolecule has been taken as 12 A.^{2}.

The fact that Σ_2 agrees well with values obtained by Gregg's method whereas $\Sigma_1 < \Sigma_2$ affords, in

SURFACE AREA OF DRY, ASH-FREE COAL (m.^{2}/gm.)

Adsorbent	Σ_1	Σ_2	Σ_3	Σ_4
Bacchus Marsh lignite, Victoria	269	357	385	270
Yallourn lignite, Victoria	250	348	388	235
Koeflach lignite, Austria	273	332	334	270
Salt Range lignite, Pakistan	146	197	198	130

itself, a tacit indication of a deficiency in the Brunauer–Emmett–Teller treatment. The point can, however, be checked by resorting to measurements of the heats of wetting of the lignites in methanol and converting heat releases to surface areas by means of Maggs's equivalent[4], 1 m.$^2 \equiv 0.1$ calorie. The resultant values, reproduced in the table as Σ_3, are in excellent agreement with those of Σ_2.

At the present stage of the investigations, one cannot be certain about the nature of the deficiency in the Brunauer–Emmett–Teller method; it may arise from the fact that the method was originally worked out in a narrow (and very low) temperature region. In any event, this view is supported by the observation that the tangent to the point of intersection of the two isotherm branches leads to a value of Σ that is virtually identical with the Brunauer–Emmett–Teller estimate (cf. Σ_4 in the table). In other words, the intercept of the tangent on the s-co-ordinate (equivalent to the intercept on this co-ordinate of the projected linear portion of a normal sigmoid isotherm) appears to provide the numerical solution to the Brunauer–Emmett–Teller monolayer equation. It follows, therefore, that in those instances in which the slope of the linear portion of a sigmoid isotherm increases with temperature, the Brunauer–Emmett–Teller method will only yield reliable results at very low temperatures (where the tangent to the point of intersection of the isotherm branches or the linear portion of a sigmoid isotherm would both run approximately parallel to the pressure axis).

It is hoped to present a fuller discussion of these considerations, and a more rigid analysis of the problem, elsewhere in due course.

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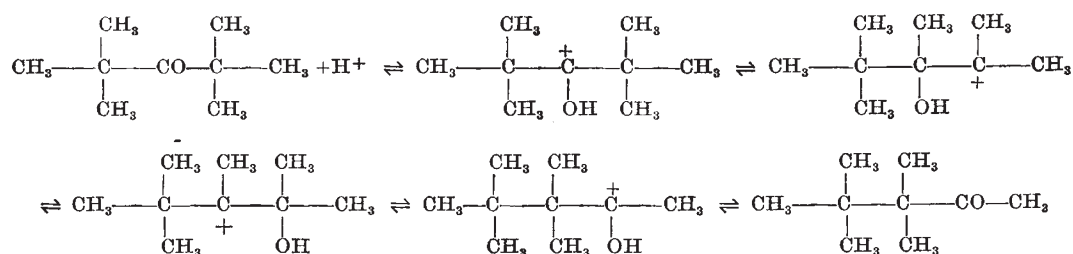[2] Berkowitz, N., and Schein, H. G., *Fuel* [31, 19 (1952)].
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Rearrangement of Hexamethyl Acetone

DURING the course of recent studies concerned with the alkylation of *iso*paraffins, in which hexamethyl acetone was used as one of the reagents, an interesting rearrangement of this ketone was observed. Hexamethyl acetone, benzene, and sulphuric acid (s.g. 1·84) were stirred together at room temperature for 24 hr.; the resulting material was purified by distillation and recrystallization. The product of the reaction was shown to be a mixture of the original ketone and 3 : 3 : 4 : 4-pentan-2-one. The following mechanism is suggested :

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CO-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 +H^+ \rightleftharpoons CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{+}{\underset{\underset{OH}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \rightleftharpoons CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{+}{\underset{}{\overset{\overset{CH_3}{|}}{C}}}-CH_3$$

$$\rightleftharpoons CH_3-\overset{+}{\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \rightleftharpoons CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{+}{\underset{\underset{OH}{|}}{C}}-CH_3 \rightleftharpoons CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CO-CH_3$$

Further work on this rearrangement is in progress.

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An Improved Hydrolytic Procedure for Urinary Neutral 17-Ketosteroids

RESEARCH on the excretion of urinary steroids has been handicapped by the lack of a procedure for hydrolysing steroidal conjugates without simultaneous partial destruction or transformation of the released steroids. We have therefore compared the urinary neutral 17-ketosteroids obtained by various methods of hydrolysis and extraction (for example, Talbot et al.[1], Hamburger[2], Beher and Gaebler[3]).

The methods were evaluated by photometric determinations of two groups of released steroids, namely, the total amount of neutral 17-ketosteroids as determined by the modification of Callow et al.[4] of Zimmermann's reaction, and the dehydroiso-androsterone fraction, a subdivision of the neutral 17-ketosteroids, as determined by the D-reaction (Jensen[5]).

Two of the seven hydrolytic procedures studied were found to be equally good. They gave a higher yield, especially of the dehydroisoandrosterone fraction, than did the other methods. In one of these two procedures use was made of simultaneous benzene extraction[2]; in this the urine aliquot is charged with one-tenth of its volume of 40 per cent by volume sulphuric acid and benzene and heated under a reflux condenser for 30 min. The other procedure was the routine method of this laboratory, and is as follows : to 1/200th of a 24-hr. urinary sample is added 1/10th volume of 70 per cent by volume sulphuric acid, after which the solution is heated to 100° C. for 30 min., cooled and extracted with ethyl ether.

Certain observations suggested that these two methods also involved a certain amount of destruction of steroids.

Talbot et al.[6] and Bitman and Cohen[7] have demonstrated that some of the neutral 17-keto-steroidal conjugates extracted from urine with n-butanol undergo hydrolysis when heated for 4 hr. to 100° C. in a buffer solution of pH 5·5–6·0. As to dehydroisoandrosterone, no destruction or trans-formation occurred.

In our investigations, aliquots of urinary specimens were adjusted to pH 3, 5, 7, 9 and 11 respectively and heated to 100° C. for 2, 4, 6, 8, 14, 30 and 48 hr. After heating for 8 hr., the steroids released from the two above-mentioned fractions reached a maximum that persisted unchanged for a further 40 hr. heating. Variations of the pH between 3 and 11 are thus of no importance so far as some of the steroidal con-jugates are concerned.

The pH of the urinary specimens received at this laboratory ranged between 4 and 10 ; most of them were acid. We therefore devised the following tech-nique. Aliquots of urine were heated to 100° C. overnight and extracted with ethyl ether. The ether extracts were then purified in the usual manner and subjected to an additional washing with 2 N sulphuric acid. The extracted urine aliquots were then hydrolysed in the routine manner described above.

Twenty urinary specimens, mostly from patients with symptoms suggesting some endocrinic dys-function, showed no determinable amounts, by ethyl ether extraction and without the use of some prepara-tory hydrolysogenic method, of compounds pro-ducing a specific colour in Zimmermann's or the D-reaction.

The technique using double hydrolysis gave 100–174 per cent (average 119 per cent) neutral keto-steroids as compared with the routine hydrolytic method. The first hydrolysis gave a dehydroiso-androsterone fraction of 100–168 per cent (average 148·5 per cent) as compared with the routine hydrolytic method. The steroidal fraction released in the first hydrolysis was 23·6–60 per cent (average 49·5 per cent) of the total amount of neutral 17-keto-steroids obtained by both hydrolyses.

The dehydroisoandrosterone fraction amounted to 0–96·6 per cent (average 66·0 per cent) of the steroidal fraction released by the first hydrolysis and 0–56·9 per cent (average 32·7 per cent) of the neutral 17-keto-steroids obtained by both hydrolyses.

Observations recorded in the literature of the hydrolysis of urinary conjugates of neutral 17-keto-steroids, and our own results, suggest that (a) the steroids released in the first hydrolysis are unsaturated and have been conjugated as sulphates ; and (b) that the fraction of steroids producing a specific colour in the D-reaction consists of steroids with a double bond connected to an angular carbon atom.

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