94. *Interaction of Ketones, Carbon Monoxide, and Steam.*

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Organic acids have been obtained from acetone and methyl ethyl ketone by high-pressure treatment with carbon monoxide and steam in presence of phosphoric acid. It is shown that the ketones condense to mesityl oxide and homomesityl oxide, respectively, which undergo hydrolytic fission into lower acids and olefins. In presence of carbon monoxide these olefins pass mainly into higher acids, but in absence of that gas they undergo polymerisation. Consideration is given to the possibility of preparing from acetone a liquid fuel of high octane number.

Certain aliphatic acids are obtained when alcohols and olefins are treated under pressure with carbon monoxide and steam in presence of phosphoric acid (Hardy, J., 1934, 1335; 1936, 358, 362, 364). *iso*Butyric acid was thus obtained from the two propyl alcohols and from propylene, whereas trimethylacetic and methylethylacetic acids were formed from the butanols and from Δ^2-butylene. It seemed possible that unsaturated acids of commercial importance would arise if this treatment were applied to ketones in view of their ability to react in the enolic condition. This possibility was negatived by experiment but, on the other hand, *saturated* acids were freely produced both from acetone and from methyl ethyl ketone * by a reaction of somewhat novel character. The experiments were carried out under a pressure of 200 atm., and a mixture of ketone and water vapours was led with carbon monoxide through liquid phosphoric acid at 200—210°. Acidity of the product was governed most markedly by reaction temperature, as is shown by the following data, which refer to methyl ethyl ketone :

Reaction temp.	146°	165°	169°	174°	179°	185°	191°	195°	200°	205°	210°
Acidity of product (N) ...	0·66	1·32	1·90	2·10	2·27	2·5	2·7	2·8	3·0	3·0	2·5

Acetone gave rise to a mixture of acetic and trimethylacetic acids in the approximate molecular ratio of 2 : 1. A small proportion of more complex acids was also present, together with a mixture of unsaturated neutral substances consisting chiefly of hydrocarbons. These observations find a simple and adequate explanation on the assumption that reaction proceeds by way of mesityl oxide, which undergoes hydrolytic fission into *iso*butylene and acetic acid :

$$\mathrm{2COMe_2 \longrightarrow CMe_2{:}CH\overset{H\vdots OH}{\vdots}CO{\cdot}Me \longrightarrow CMe_2{:}CH_2 + Me{\cdot}CO_2H}$$

Part of the *iso*butylene undergoes polymerisation into higher olefins, and the remainder reacts with carbon monoxide and steam in known fashion (Hardy, J., 1936, **358**, 362) :

$$\mathrm{CMe_2{:}CH_2 + H_2O + CO \longrightarrow CMe_3{\cdot}CO_2H}$$

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* The essential features of this work were completed (see British Patent Application No. 18330/2.7.1936) without knowledge of U.S.P. 2,037,684 (A. T. Larson, Assr. to E. I. Du Pont de Nemours & Co., granted, 14.4.36; date of application, 25.5.33. See *British Chemical Abstracts, B*, 417, 1937) which claims the production of acetic and trimethylacetic acids from acetone, and of unspecified acids from other ketones including methyl ethyl ketone.

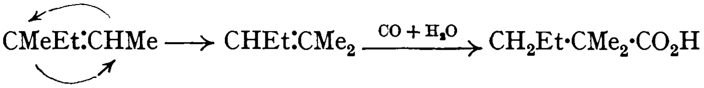
This hydrolytic fission of mesityl oxide finds a parallel in the formation of acetic and α-hydroxy*iso*butyric acids by permanganate oxidation of mesityl oxide (Pinner, *Ber.*, 1882, **15**, 591), and recalls a synthesis of the latter from *iso*butylene and acetyl chloride or acetic anhydride in presence of aluminium and zinc halides (Kondakow, *J. Russ. Phys. Chem. Soc.*, 1894, **26**, 12, 232; Krapiwin, *Chem. Zentr.*, 1910, I, 1336). Confirmation of the foregoing mechanism has been obtained by treating mesityl oxide with carbon monoxide and steam in presence of phosphoric acid, acetic and trimethylacetic acids being readily obtained. Moreover, if hydrogen or nitrogen be employed in place of carbon monoxide, acetone yields acetic acid together with an increased amount of neutral unsaturated oil, this reaction being independent of pressure. In absence of carbon monoxide, therefore, formation of trimethylacetic acid is impossible, and the only course of reaction left open to the *iso*butylene is polymerisation. Attempts to isolate *iso*butylene itself as a product of reaction have been unsuccessful, so it would appear that the conditions necessary for bringing about hydrolytic fission are too severe to allow the survival of the olefin.

When methyl ethyl ketone was treated with carbon monoxide, acids and unsaturated neutral oils were again produced. The acid mixture was, however, more complex, and the following constituents have been identified: acetic, propionic, αα-dimethylbutyric ($CMe_2Et{\cdot}CO_2H$), αα-dimethylvaleric ($CMe_2Pr{\cdot}CO_2H$), and α-methyl-α-ethylbutyric ($CMeEt_2{\cdot}CO_2H$). Acetic acid and the two heptoic acids constituted the bulk of the mixture and can only have been produced by hydrolytic fission of γδ-dimethyl-Δ^{γ}-hexen-β-one:

$$2COMeEt \longrightarrow CMeEt{:}CMe\overset{H\,\vdots\,OH}{-\vdots-}COMe \longrightarrow CMeEt{:}CHMe + Me{\cdot}CO_2H$$

$$CMeEt{:}CHMe + CO + H_2O \longrightarrow CMeEt_2{\cdot}CO_2H$$

The formation of αα-dimethylvaleric acid definitely involves a molecular transformation which is most likely to occur by isomerisation of γ- into β-methyl-Δ^{β}-pentene:



$$CMeEt{:}CHMe \longrightarrow CHEt{:}CMe_2 \xrightarrow{CO + H_2O} CH_2Et{\cdot}CMe_2{\cdot}CO_2H$$

Such a rearrangement involving the exchange of an alkyl group for hydrogen across an unsaturated link has already been encountered in this series of experiments (J., 1936, 362, 364, and unpublished observations) and it would now appear that it is of the Wagner–Meerwein type.* The two remaining acids, propionic and αα-dimethylbutyric, must on the other hand have been formed from γ-methyl-Δ^{γ}-hepten-ε-one:

$$2COMeEt \longrightarrow CMeEt{:}CH\overset{H\,\vdots\,OH}{-\vdots-}CO{\cdot}Et \longrightarrow CMeEt{:}CH_2 + Et{\cdot}CO_2H$$

$$CMeEt{:}CH_2 + CO + H_2O \longrightarrow CMe_2Et{\cdot}CO_2H$$

so it is fairly evident that, in presence of phosphoric acid under the experimental conditions, methyl ethyl ketone condenses with itself to give a mixture of dimethylhexenone and methylheptenone in which the former predominates. This conclusion is in agreement with the observations of Abbott, Kon, and Satchell (J., 1928, 2514), who found that acid catalysts favour the formation of dimethylhexenones whereas alkaline agents lead to methylheptenones (cf. Powell and Secoy, *J. Amer. Chem. Soc.*, 1931, **53**, 765; Grignard and Cologne, *Compt. rend.*, 1930, **190**, 1349).

Attempts to apply this process to other ketones have so far met with little success. No acid could be obtained from *cyclo*hexanone, whereas diethyl ketone gave in very small yield a mixture of propionic acid and an unidentified heptanoic acid instead of the anticipated octanoic acid. Evidently the olefin derived by hydrolytic fission of δ-methyl-ε-ethyl-Δ^{δ}-hepten-γ-one had lost a methyl group in exchange for a hydrogen atom:

$$2COEt_2 \longrightarrow CEt_2 = CMe\overset{H\,|\,OH}{-|-}COEt \longrightarrow CEt_2{:}CHMe + Et{\cdot}CO_2H$$

probably by interchange with another molecule:

$$2CEt_2{:}CHMe \longrightarrow CEt_2{:}CH_2 + CEt_2{:}CMe_2$$

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* Grateful acknowledgment is made to Professor J. Kenner, who advanced this suggestion at a lecture given by the author in Manchester on October 2nd, 1936.

but the amount of material was inadequate for a full investigation of this matter. The existence of such an olefinic interchange has been demonstrated in the case of the amylenes (unpublished observation) by the isolation of acids with one more and one less carbon atom than that which would be produced by normal reaction with carbon monoxide and steam.

The production of trimethylacetic acid from acetone demonstrated the transient existence of *iso*butylene and directed attention to the possibility of producing a fuel of high octane number from acetone by treatment with steam in presence of phosphoric acid and an inert gas such as nitrogen or hydrogen. Hydrogenation of the neutral unsaturated material so obtained yielded a spirit fraction (b. p. $<200°$) which had an octane number of 81 and was miscible with ordinary motor spirit. This relatively low octane number is a little surprising in view of the fact that the material has its origin in *iso*butylene, but the conditions of polymerisation are severe and may lead to hydrocarbons with poor anti-detonation characteristics. This suggestion has already been advanced by Ipatieff and Komarewsky (*Ind. Eng. Chem.*, 1937, **29**, 958) to account for the low octane numbers (83 and 84) of octane fractions (b. p. 100—125°) obtained by simultaneous polymerisation and hydrogenation of *iso*butylene in presence of a phosphoric acid–iron–nickel oxide catalyst at 250° and 300°.

EXPERIMENTAL.

The apparatus and experimental technique were substantially as described previously (J., 1934, 1339), and 400 c.c. of 87% phosphoric acid were employed uniformly as catalyst. Except where otherwise stated, the pressure was 200 atm. and the rate of circulation was 40 l. of compressed gas per hour.

The products were worked up according to the following procedure, designed to permit an almost complete recovery of anhydrous acids. After addition of slightly more than the theoretical quantity of potassium hydroxide solution (50%), the products were distilled to remove unchanged ketone. Residual oil was separted from the aqueous solution of salts, and the latter was evaporated to dryness and dried in a vacuum at 200°. A considerable excess of anhydrous phosphoric acid was then added to the dry salts, and the liberated acids were recovered by distillation (oil-bath) first under ordinary and then under reduced pressure. The acid distillate still contained a small amount of water which was removed by azeotropic distillation with benzene, and the anhydrous acids were distilled fractionally through a 4′ electrically-heated Dufton column.

Acetone and Carbon Monoxide.—A mixture of acetone (1450 g.) and water (362 g.) was injected into the vaporiser at the rate of 280 c.c. per hour, and at a reaction temperature of 200—205° gave a product (1720 g.; C, 49·4; acidic H, 0·47%) from which unchanged acetone (514 g.) and unsaturated oil (188 g.; C, 85·1; H, 11·2%) were isolated. From these data the carbon balance (in g.) could be calculated :

Carbon introduced as acetone	900	—
,, ,, CO (estimated)	32	—
Carbon accounted for as recovered acetone	—	319
,, ,, acids	—	371
,, ,, neutral oils	—	160
,, ,, substances scrubbed from the waste gases by conc. H_2SO_4	—	21·5
Loss	—	60·5
Total	932	932

The acids (550 g.) were distilled as follows :

B. p.	116—125°	125—155°	155—161°	161—164°	164—166°	166—170°	170—185°	Residue
Weight (g.)	262·5	9·4	1·3	33·3	196	13·7	6·8	27

The fraction of b. p. 116—125° was acetic acid and gave *p*-phenylphenacyl acetate, m. p. 109—109·5° and mixed m. p. 110°. The fraction, b. p. 164—166°, which crystallised on cooling, was shown to be trimethylacetic acid by conversion into its anilide, m. p. and mixed m. p. 132—133°.

Mesityl Oxide and Carbon Monoxide.—The vaporiser was initially filled with water, heated to 110°, and mesityl oxide was injected at the rate of 220 c.c. per hour. At a reaction temperature of 200° the product was homogeneous and contained 0·54% of acidic hydrogen. After neutralisation, 1122 g. of product gave a distillate, the upper layer of which was re-distilled :

B. p.	$<80°$ (A)	80—100° (B)	100—140° (C)	Residue (D)
Weight (g.)	13	33	236	135

A, B, and C consisted respectively of acetone, the constant-boiling mixture of mesityl oxide and water (b. p., *ca.* 92·2°), and mesityl oxide (Found : C, 73·4; H, 10·1. Calc. for $C_6H_{10}O$: C, 73·5; H, 10·2%). The residue from the first distillation consisted of an upper layer of dark oil (58·5 g.; C, 80·7; H, 11·1%) and an aqueous solution of salts, from which 318 g. of acids were isolated :

B. p.	117—125°	125—141°	141—160°	160—163°	163—165°	Residue
Weight (g.)	193	2·5	4	19	73	23·5

The fraction of b. p. 117—125° was acetic acid (*p*-phenylphenacyl acetate, m. p. and mixed m. p., 109·5—110°), and that of b. p. 163—165° was trimethylacetic acid, which crystallised on cooling and was identified by conversion into anilide, m. p. 130—130·5° and mixed m. p. 130·5—131°.

Methyl Ethyl Ketone and Carbon Monoxide.—In 6 hours a mixture of methyl ethyl ketone (1042 g.) and water (116 g.) was vaporised and led with carbon monoxide through the catalyst at 200°. The product (1253 g.) consisted mainly of an upper layer (1070 g.; C, 56·5; acidic H, 0·33%), together with a small lower layer (183 g.; C, 15·1%). After small samples had been taken for analysis, the product (1065 g. of upper, and 181·7 g. of lower layer) was made alkaline and was distilled up to 85° to remove the binary mixture of methyl ethyl ketone and water (597 g.; C, 60·15%). Further distillation, with addition of water when necessary, gave a steam-volatile oil (58·3 g.; C, 77·6; H, 11·6%), and a residual non-volatile oil (38·3 g.; C, 80·5; H, 11·4%) was extracted with petroleum (b. p. 40—60°) from the aqueous solution of salts. These data lead to the following carbon balance (in g.) :

Carbon introduced as COMeEt	695	—
,, ,, CO (estimated)	20	—
Carbon accounted for as recovered COMeEt	—	364
,, ,, oil (steam-volatile)	—	45·4
,, ,, oil (non-volatile)	—	31
,, ,, acids	—	192·6
,, ,, products scrubbed from exit gases by conc. H_2SO_4	—	45
Loss	—	37
Total	715	715

From the dried potassium salts, 315 g. of anhydrous acids were isolated, and were separated into the following fractions :

B. p.	<115°	115—123°	123—136°	136—144°	144—175°	175—180°
Wt. (g.)	6·2	81·5	7·9	20·9	22·8	2·4
B. p.	180—190°	190—195°	195—202°	202—210°	Residue	
Wt. (g.)	39·4	13·0	34·8	46·4	28·1	

The fraction of b. p. 115—123° was shown to be acetic acid by conversion into *p*-phenylphenacyl acetate, m. p. and mixed m. p. 109°, whereas that of b. p. 136—144° was propionic acid (Found : equiv., 75. Calc. : equiv., 74). It was identified by means of its *p*-phenylphenacyl ester, m. p. 96° and mixed m. p. with an authentic specimen (m. p. 100°) 98—99°. The fraction of b. p. 182—190° (Found : equiv., 114. Calc. for $C_6H_{12}O_2$: equiv., 116) contained αα-dimethylbutyric acid and was converted into amide (m. p. 101°; mixed m. p. 102—103° with authentic material of m. p. 102—103°), anilide (m. p. 89°; mixed m. p. 90·5—91°), and *p*-phenylphenacyl ester (m. p. 82—84°). Wrede and Rothhaus (*Ber.*, 1934, **67**, 739) give 86·5° as the m. p. of *p*-phenylphenacyl αα-dimethylbutyrate. The material, b. p. 202—210°, contained two difficultly-separable heptoic acids (Found : equiv., 131. Calc. : equiv., 130), the amides of which differed markedly, one crystallising in plates and the other in needles. By careful fractional distillation of a greater quantity, the material was divided into fractions as follows :

B. p.	200—202°	202—205°	205—207°	207—208·4°	208·4—208·6°	Residue
Wt. (g.)	2·5	28·9	60·7	58·8	6·9	8·0

The acid of b. p. 202—205° gave an amide which crystallised from petroleum (b. p. 40—60°) in plates, m. p. 93—94°, and did not depress the m. p. of authentic αα-dimethylvaleramide (m. p. 94·5°). Fraction b. p. 208·4—208·6° was shown to be α-methyl-α-ethylbutyric acid by preparing the amide [needles, m. p. 74—75°; mixed m. p. with authentic material (m. p. 75·5—76°) 74—75·5°] and anilide [needles from petroleum (b. p. 60—80°), m. p. 84—85°; mixed m. p. 85—86° with an authentic specimen of m. p. 87—87·5°].

Diethyl Ketone and Carbon Monoxide.—In this experiment the vaporiser was filled with water and heated to 100°. Diethyl ketone was then pumped in at the rate of 160 c.c. per hour. The resulting vapours were led with carbon monoxide through the catalyst whose temperature was gradually raised from 190° to 290°. At intervals the product was withdrawn, and titrated with standard alkali:

Reaction temp.	189°	199°	204°	212°	225°	233°	241°	250°	260°	276°
Acidity (N)	0·26	0·39	0·42	0·51	0·65	0·67	0·53	0·65	0·51	0·37

The acids from the combined material were distilled as follows:

B. p.	<136°	136—143°	143—160°	160—215°	215—220°	220—225°	Residue
Wt. (g.)	0·5	6·3	5·3	1·0	4·6	2·0	3·4

The acid of b. p. 136—143° gave an anilide, m. p. and mixed m. p. with authentic propionanilide, 104°. The acid of b. p. 215—220° (Found: equiv., 133, 134. Calc. for $C_6H_{13}·CO_2H$: equiv., 130) gave an anilide which crystallised from light petroleum (b. p. 40—60°) in colourless needles, m. p. 92—94°, and after recrystallisation the first fraction melted sharply at 110°. It also gave a very soluble anilide, obtained as colourless needles, m. p. 86—89°, from petroleum (b. p. <40°).

Acetone and Nitrogen.—A mixture of acetone and water (4 : 1 by wt.) was injected into the vaporiser at 95°, and the vapours were led with nitrogen under 120 atm. through the catalyst at 200—205°. The product consisted of an upper yellow-brown oil and a lower acidic layer, and the ratio of upper to lower layer varied from 1 : 5 to 1 : 3 by volume. The total product (1262 g.) contained 319 g. of upper layer (C, 85·5, 85·7; H, 12·4, 12·3%) and 943 g. of lower layer (C, 40·4, 40·2; H, 10·1, 10·4; acidic hydrogen, 0·33%, *i.e.*, acetic acid, 19·8%). The lower layer (909 g.) was neutralised with potassium hydroxide and distilled up to 80°, unchanged acetone (477 g.) being recovered. It was substantially free from hydrocarbons since, on dilution, no upper layer separated. The residue from the distillation contained a very small upper layer which was volatile in steam and appreciably soluble in water (mesityl oxide ?). From the salts, acetic acid (70 g. of b. p. 117—120°) was isolated and identified by conversion into *p*-phenylphenacyl acetate, m. p. 107—108°, mixed m. p. 107—108·5°. The oily upper layer (291 g.) was dried and neutralised over potassium hydroxide and then distilled to 75° to remove acetone (35 g.). The residue was distilled:

B. p.	—100°	100—150°	150—200°	200—250°	250—315°	Residue
Wt. (g.)	negligible	8·8	32	86·1	87·6	16

The material, b. p. 100—315°, was catalytically hydrogenated in presence of nickel–kieselguhr at 200° and at 100 atm. (initial). Absorption of hydrogen was slow. The product was separated by distillation into fractions, the properties of which were as follows:

			Composition.	
Fraction.	%.	$d^{24°}$.	C, %.	H, %.
<100°	3·5	—	—	—
100—150	3·7	0·737	81·8	14·5
150—200	8·3	0·797	84·5	13·5
200—250	37·9	0·839	85·3	12·9
250—300	38·0	0·893	86·3	12·2
Residue	8·6	—	—	—

Similar products were obtained by working at 30 atm. and at 10 atm.

Acetone and Hydrogen.—The vapour from 80% acetone was led with hydrogen under 30 atm. through the catalyst at 200—220°. Starting with 5228 g. of acetone, 2180 g. of which were recovered and resubmitted to the catalyst, 1650 g. of oil were obtained. The portion of the oil boiling below 185°/100 mm. was exhaustively treated with hydrogen under 120 atm. (initial) in presence of nickel–keiselguhr catalyst, and the resulting material was distilled up to 200°. The distillate had a sweet and pleasant odour unlike that of petrol. It had $d^{20°}$ 0·775, and octane number 81.

Authentic Specimens.—$\alpha\alpha$-Dimethylbutyric, $\alpha\alpha$-dimethylvaleric and α-methyl-α-ethylbutyric acids were prepared by hydrolysing with 25% sulphuric acid the amides formed from the appropriate $\omega\omega\omega$-substituted acetophenones by treatment with sodamide (Haller and Bauer, *Compt. rend.*, 1909, **148**, 70). The substituted acetophenones were prepared by alkylating *iso*- or *n*-butyrophenone (*idem, ibid.*, p. 129). Two of the anilides had not hitherto been prepared. $\alpha\alpha$-*Dimethylvaleranilide* (Found: N, 6·83. $C_{13}H_{19}ON$ requires N, 6·83%) and α-*methyl*-α-*ethylbutyranilide* (Found: N, 6·83%) crystallised in needles, m.p. 73·5° and 87—87·5° respectively.

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