Syntheses of Aliphatic Dibasic Acids from Paraffinic Hydrocarbons by Way of Auto-oxidation in Systems Containing Water[*1]

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(Received February 5, 1962)

Several attempts have been made to obtain dibasic fatty acids by the direct oxidation of paraffinic hydrocarbons with molecular oxygen; for instance, Zellner and Lister¹⁾ obtained a distillate fraction of succinic acid to sebacic acid in a yield of 20～25% against the amount of reactant consumed in the oxidation of the scale waxes. In this investigation, the oxidation by air or oxygen was carried out at 150°C, employing a catalyst composed mainly of manganese salt; Zellner and Lister have stated that the reaction was inhibited during the course of oxidation due to the lactone-like polymers produced secondarily, leading to the cessation of the reaction at an early stage of oxidation. In order to attain a deep oxidation without a decrease in the reaction velocity in the later stage, many counterplans have been proposed, such as strict control²⁾ of the reaction temperature and of the depth of oxidation, and employment of effective cocatalysts³⁾. However, the yield of the object materials, crystalline dibasic acids (C_4-C_{10}), has been low so far. Recently, however, Tsyskovskii et al.⁴⁾ repeated the investigation of Zellner and Lister in an attempt to improve the yield of crystalline dibasic acids; they obtained a fraction of succinic acid—sebacic acid in a yield of 40% against the charged starting material by oxidizing liquid paraffin of a high boiling point and by then hydrolyzing the reaction products at 160°C and 15 atm.

One of the present authors has reported⁵⁾ that dibasic acids can be obtained by the auto-oxidation of long chain aliphatic monobasic acids or aliphatic hydrocarbons in the presence also of water. For this paper, this method of reaction has been extended to the oxidation of *n*-decane and solid paraffin; the results obtained are compared with those for the oxidation of anhydrous decane and other former studies, and the effect of water is discussed.

Experimental

Apparatus, Procedure and Materials.—The apparatus used for the oxidation reaction is a vertical autoclave (made of SUS-32) 355 cc. in capacity and with a magnetic stirrer. The reaction temperature was maintained constant within ±0.5°C.

Hydrocarbons and water were charged into the autoclave and, while being stirred, were heated to a desired temperature. Then, after the total pressure had been read, oxygen was introduced until a desired pressure was reached; the depression of the pressure with time was followed at the constant temperature. The rate of the revolution of the stirrer was kept at about 600 r. p. m. to prevent the dissolution of oxygen from becoming a limiting factor for the overall reaction velocity. The total pressure (gauge reading) was kept in a range of 20～80 kg./cm² during the reaction.

After the reaction had been stopped by cooling the autoclave, the residual gas, collected in a trap in a dry ice-methanol bath, was subjected to gas analysis. In this experiment, only a trace of condensate was found in the cold trap. The liquid products were taken out, treated according to a method described later, and subjected to analysis.

The *n*-decane used was prepared⁶⁾ from commercial *n*-decanol-1; it showed a b. p. of 174～175°C and a purity of 99.5～99.7% (in analysis by gas chromatography). Commercial solid paraffin (m. p., 60°C) and oxygen gas in a cylinder (purity, 99.6～99.7%) were used without further purification.

After-treatment and Method of Analysis.—The carbon dioxide, oxygen, carbon monoxide and unsaturated as well as saturated hydrocarbons in the gaseous product were immediately analyzed according to the usual method employing Hempel's apparatus; in some cases, analysis by gas chromatography was also applied. In order to estimate quantitatively each of the acidic constituents in the liquid product, the reaction product was after-treated according to the scheme summarized in Fig. 1, and gas chromatagraphic analysis[*4] was applied to each fraction.

A liquid reaction product was filtered through a wet filter paper, rinsed with water, and divided

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[*1] Partly pressented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

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1) C. N. Zellner and F. Lister, *Ind. Eng. Chem.*, **48**, 1938 (1956).

2) J. P. Buckmann, U. S. Pat. 2729655 (1956).

3) C. N. Zellner and F. Lister, U. S. Pat. 2841603 (1958).

4) V. K. Tsyskovskii, M. I. Levina, B. G. Freidin and V. P. Leont'eva, *Khim. Prom.*, **1960**, 272.

5) M. Kobayashi, *Abura Kagaku*, **9**, 314 (1960).

6) S. Kudo, K. Shimomura and K. Negishi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 1372 (1962).

[*4] Perkin-Elmer Model 154 B

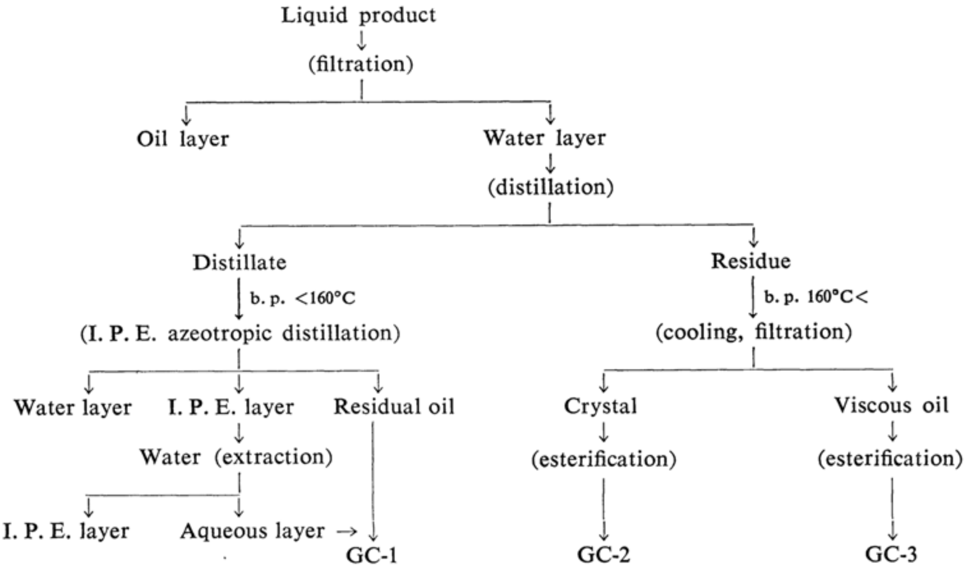

Fig. 1. After-treatment of the liquid product.

into an oily layer and an aqueous layer. While this oily layer consisted of unchanged hydrocarbons containing a few non-acidic oxidation products, the aqueous layer contained, as main ingredients, monobasic fatty acids in addition to the desired dibasic fatty acids, and the existence of a minute amount of carbonyl compound was detected. This aqueous layer was separated by distillation into two fractions, that is, a fraction distilling below 160°C (water and C_1-C_6 monobasic acids) and a residual fraction with a boiling point higher than 160°C (monobasic acids higher than C_7, dibasic acids and other polymerized compounds).

The former fraction was subjected to azeotropic distillation with isopropyl ether (abbreviated as I. P. E. in Fig. 1) and was separated into three portions: water layer, I. P. E. layer, and residual oil. The I. P. E. layer was further extracted with water; a small amount of the acidic ingredients was recovered, added to the residual oil, and subjected directly to gas chromatographic analysis.

The latter high-boiling residue gave crystals of dibasic acids (C_4-C_6) immediately after cooling. These crystals and the highly viscous filtrate were both esterified with *n*-butanol by the aid of sulfuric acid in the usual procedure, using benzene as an accompanying agent for the water formed. Finely powdered sodium carbonate was added to the esterified product to neutralize the acidic contaminant; the solution was then filtered and vacuum distilled; colorless and clear or slightly yellow *n*-butyl esters were used, respectively, as samples for the gas chromatographic analysis.

The GC noted in Fig. 1 indicates the quantitative analysis by gas chromatography.

After-treatment was conducted in the order shown in Fig. 1; the absolute amounts of samples GC-1-GC-3 were calculated from the acid value obtained in the usual way, while the relative amount of each acidic constituent was determined by gas chromatography. The conditions for the gas chromatographic analysis were as follows: for GC-1, column OS 2 m. (dioctyl sebacate+sebacic acid)[7], 150°C, helium as the carrier gas, rate of flow, 47 cc./min.; for GC-2 and GC-3, column O 2 m. (silicon grease), 260°C, helium as the carrier gas, rate of flow, 17 cc./min.

Results

Absorption of Oxygen.—In Fig. 2 are shown examples of the time course of oxygen absoption by *n*-decane (Exp. DX-8, reaction temperature 160°C) and solid paraffin (Exp. DX-14, 150°C). Oxygen is absorbed almost linearly with time after some lapse of the induction period. These curves represent apparent pressure decreases. The true oxygen absoption curves could be almost straight lines if necessary corrections are made for carbon dioxide, carbon monoxide and other gases formed secondarily during the reaction; thus the over-all oxidation reaction may be considered to proceed in a steady state.

With the object of finding the partial pressure of oxygen necessary for maintaining the steady rate in this reaction, the reaction was allowed to proceed without any replenishment of oxygen after the start of the reaction; a gas aliquot was sampled for analysis at the point where the reaction velocity began to decrease, and the partial pressure of oxygen in the gas phase of the reaction system was calculated. The results are shown in Table I. $\rho_{\max}$ (maximum rate of oxygen absorption) and θ (induction period) in the table indicate,

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[7] S. Kudo, K. Shimomura, K. Negishi and K. Fukui, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 1379 (1962).

TABLE I. EFFECTIVE PARTIAL PRESSURE OF OXYGEN
(Amount of *n*-decane charged, 30 g. water, 70 g., reaction temperature, 160°C)

Experimental No.	θ hr.	$\rho_{\max}$ kg·cm^{-2} hr^{-1}	Oxygen pressure when $\rho_{\max}$ begins to decline: Total pressure kg./cm^2	O$_2$ Concn. vol. %	O$_2$ Partial pressure kg./cm^2
DX-4	1.1	9.0	28.0	22.7	5.3
DX-5	0.9	9.0	21.6	26.7	4.6
DX-6	0.9	9.9	16.3	47.1	6.0

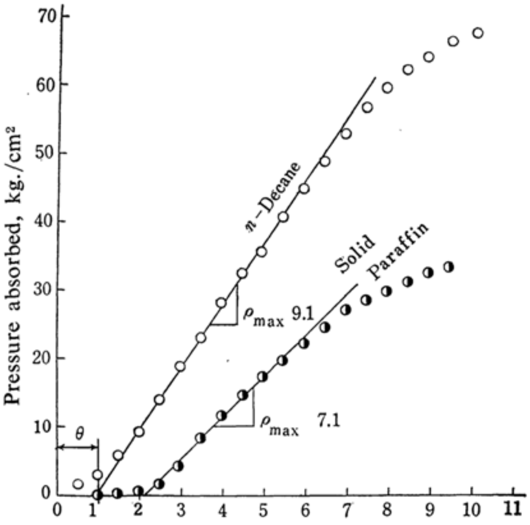

Fig. 2. Rate of oxygen absorption.

respectively $-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t$ at the linear portion of the oxygen absorption curve and the time reading at the cross point of this straight line with the abscissa, as is shown in Fig. 2.

It can be infered from the results shown in Table I that $\rho_{\max}$ becomes independent of the oxygen pressure when the effective partial pressure of oxygen is higher than 5~6 kg./cm^2 and that $P_{\mathrm{O}_2}=5\sim6$ kg./cm^2 may be taken practically as a critical value.

Oxidation Products from *n*-Decane.—*Water-soluble Products and Gaseous Products.*—In Table II are presented the experimental conditions and reaction products in the oxidation of *n*-decane under a pressure at 160°C in the presence also of water. In this table, instances for various depths of oxidation in the case of the oxidation of *n*-decane are given; from these a relation between the amount of oxygen absorbed and the amount of *n*-decane consumed was sought, resulting in a straight line, as shown in Fig. 3. The amount of *n*-decane consumed was calculated by subtracting the amount of the water-insoluble oil layer remaining after the reaction from the amount charged originally. The recovered oil layer consisted mainly of *n*-decane, besides about 10% of *n*-decanone and a small amount of lower fatty acids, as will be described later. Therefore, the oily layer was regarded as the same as the starting material, *n*-decane.

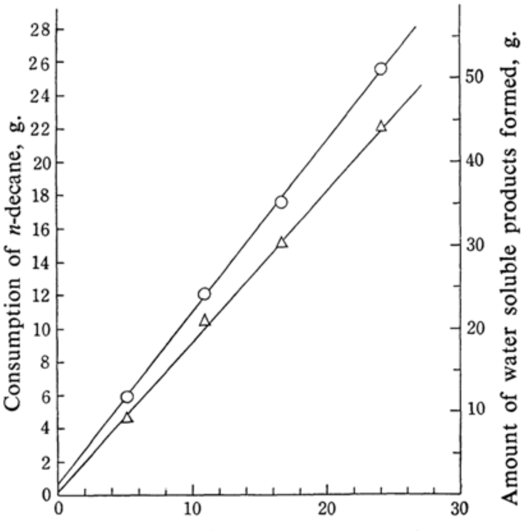

Fig. 3. Consumption of *n*-decane and amount of water-soluble products formed versus depth of oxidation.
○ Consumption of *n*-decane
△ Amount of water soluble products formed

Furthermore, the linear relation between the amount of water-soluble products and that of oxygen absorbed is also illustrated in Fig. 3. From the fact that linear relations were obtained between the depth of oxidation and the consumption of *n*-decane or the amount of water-soluble products respectively, the oxidation reaction in this system containing water may be considered as directly producing water-soluble fatty acid fractions, but not as proceeding step by step via water-insoluble neutral oxidation products.

The water layer separated from the oil layer was clear but slightly yellow, and was subjected to quantitative analysis for each fatty acid in the way cited in Fig. 1; the results are shown in Table II. When the water-soluble products were treated in order of Fig. 1, and the residue of higher boiling point than 160°C was esterified and then vacuum destilled, there

TABLE II. OXIDATION OF *n*-DECANE

Experimental No.	DX-9		DX-7		DX-10		DX-8	
Amount of *n*-decane charged, g.	30		30		30		30	
Amount of water charged, g.	70		70		70		70	
Reaction temp., °C	160		160		160		160	
Total reaction press., kg./cm^2	16～40		28～60		22～60		30～60	
Reaction time, hr.	2.6		5.0		7.6		10.3	
$\rho_{\max}$, kg. cm^{-2} hr^{-1}	9.0		9.0		9.1		9.1	
θ, hr.	0.9		1.0		0.8		0.9	
Amount of oxygen absorbed, g.	6.9		15.5		23.3		34.6	
Amount of *n*-decane consumed, g.	6.9		12.0		17.5		25.5	
Products in aqueous layer								
	g.	wt. %	g.	wt. %	g.	wt. %	g.	wt. %
Formic acid	0.04	0.5	0.5	4.3	0.85	4.4	0.55	1.9
Acetic acid	2.09	25.5	4.22	36.3	7.31	37.9	14.30	49.4
Propionic acid	1.02	12.4	1.29	11.1	1.92	10.0	2.93	10.1
n-Butyric acid	0.55	6.7	1.08	9.3	1.85	9.6	1.29	4.5
n-Valeric acid	0.21	2.6	0.30	2.6	0.49	2.5	0.90	3.1
Caproic acid	0.06	0.7	0.08	0.7	0.18	0.9	0.19	0.7
Heptanoic acid	1.02	12.4	0.88	7.6	1.72	8.9	1.15	4.0
Caprylic acid	0.62	7.5	0.39	3.3	0.56	2.9	0.17	0.6
Pelargonic acid	0.39	4.7	0.28	2.4	0.26	1.4	0.03	0.1
Succinic acid	1.89	23.0	2.06	17.7	2.91	15.1	5.49	19.0
Glutaric acid	0.28	3.4	0.42	3.6	0.97	5.0	1.59	5.5
Adipic acid	0.05	0.6	0.06	0.5	0.12	0.6	0.26	0.9
Pimelic acid	0	0	0.01	0.1	0.16	0.8	0.02	0.1
Suberic acid	0	0	0.06	0.5	0	0	0.02	0.1
Azelaic acid	0	0	trace		0	0	0	0
Total	8.22	100.0	11.63	100.0	19.3	100.0	28.89	100.0
Gaseous products								
CO_2	1.44 g.		4.19 g.		8.48 g.		17.43 g.	
CO	0.15 g.		0.39 g.		0.74 g.		1.36 g.	
C=O	0		trace		0		trace	
Others	0.24 l.		0.52 l.		0.75 l.		1.31 l.	

remained only a small amount (0.2～0.5%) of the residue of distillation (probably polymers of the lactone series) in each experiment listed in Table II. Thus, it can be said that the formation of products which look like polymers of the lactone series is not remarkable in this oxidation procedure.

Furthermore, the gas chromatograms of the samples GC-1-GC-3 obtained by the treatment shown in Fig. 1 were compared precisely, with respect to the retention time, with each standard specimen of the fatty acids, but no peak other than that of the fatty acids was noticed. Thus, the main reaction products in this oxidation reaction can be concluded to be a mixture of fatty acids.

Immediately after the reaction was stopped, both oil and water layers were examined for hydroperoxide (expressed as HPO hereafter), but only a trace was found in each experiment cited in Table II.

As aqueous products, the monobasic fatty acids C_1—C_9 and the dibasic fatty acids C_4—C_7 were obtained; the dibasic acids C_8—C_9 were found only in traces, as is shown in Table II. In order to realized the relation between the depth of oxidation and the formation of each fatty acid, the sum of the monobasic acids C_7—C_9 (cited as higher monobasic acids), the sum of the dibasic acids and the amount of acetic acid formed are plotted against the depth of oxidation in Fig. 4.

The ratio of the amount of dibasic acids consisting mainly of succinic acid to the total acidic ingredients was 22～27%, which can be regarded as nearly constant irrespective of the depth of oxidation. On the other hand, the content of higher monobasic acids decreased, while that of acetic acid increased with the depth of oxidation. Finally it seemed that the aqueous constituents became succinic acid and acetic acid; for instance, in Exp. DX-8

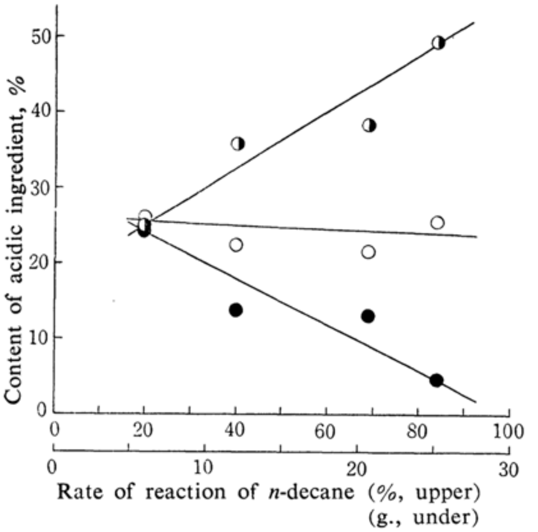

Fig. 4. Depth of oxidation—acidic ingredients.

○ Dibasic acid ◑ Acetic acid
● Higher monobasic acid

of Table II, acetic acid was found to form 49%, succinic acid, 19%, and their sum, 68% at a 85.6% consumption of *n*-decane.

As is shown in Table II, gaseous products consisted mainly of carbon dioxide, together with a small amount of carbon monoxide and a trace of lower olefinic hydrocarbons (shown as C=C in Table II and hereafter).

In order to investigate the other gaseous ingredients, gas chromatographic analysis was conducted on the residual gas in Exp. DX-10 of Table II as an example; the results showed a composition: H_2, 42; CH_4, 4; H_2, 54%. It was also found that hydrogen formed more than 40%. It has not yet been elucidated how this hydrogen is produced, but perhaps it did so in a reaction which can be formulated by the following equation:

$$RCH_2OOH \rightarrow RCOOH + H_2$$

in which prim-HPO is thermally decomposed directly into fatty acids and hydrogen[8]; a mechanism analogous to this may also be interpreted to be operating.

Cleavage of Carbon Chains.—In view of the fact that acetic acid, carbon dioxide and carbon monoxide increase rapidly with the progress of oxidation, as may be seen from the experimental results in Table II, the relation between acetic acid and these gaseous constituents was investigated. As is seen in Fig. 4 and as has been described above, the ratio of the rate forming dibasic acids to the total rates forming all products appears constant, irrespective of the depth of oxidation, whereas the increase in the amount of acetic acid in the range of deep oxidation, contrary to the decrease in the amount of higher monobasic acids, suggests that acetic acid may be formed by a cleavage of the carbon chain of higher monobasic acids. Therefore, the competitive occurrence of the following three elementary steps, A, B_1 and B_2, were assumed to contribute to the overall oxidation reaction:

$$n\text{-Decane} \rightarrow \text{acetic acid} + \text{dibasic acid} + CO_2,\ CO \qquad (A)$$

$$n\text{-Decane} \rightarrow \text{acetic acid} + \text{higher monobasic acid} + CO_2,\ CO \qquad (B_1)$$

$$\text{Higher monobasic acid} \rightarrow \text{acetic acid} + CO_2,\ CO \qquad (B_2)$$

In addition to these steps, other processes, such as the formation of HPO, keto-acid, alcohol and hydroxy-acid as intermediate products, the formation of dibasic acids from higher monobasic acids (perhaps Reaction A proceeds via higher monobasic acids intermediately), and the oxidative decomposition of higher dibasic acids to lower dibasic acids, are also conceivable, but Reactions A, B_1 and B_2 were taken as representative.

Assuming that Reaction A is a normal reaction yielding dibasic acids, and that B_1 and and B_2 represent reactions to shorten carbon chains, it seems probable that B_1 contributes in the early stage of oxidation and that B_2 becomes important in the range of deep oxidation. Thus, if Reaction A actually competes with Reaction B_1, as above, the amount of acetic acid and gaseous constituents found should maintain a constant ratio to the amount of dibasic acids, and the rapid increase of the former in the range of the deeper degree of oxidation is wholly due to reaction B_2. It was established by the experimental results in Table II that this was the case. Experiment DX-9 of shallow oxidation (conversion of *n*-decane, 20.0%) was thought to proceed by way of Reaction A, without any contribution of Reaction B_1 or B_2, until this extent of reaction. Thus, the ratio of each amount of acetic acid (35 mmol.), carbon dioxide (34 mmol.) and carbon monoxide (5.5 mmol.) to the amount of dibasic acids (18 mmol.) obtained in this experiment was assumed to be the normal ratio of production by Reaction A. The increase in the amount of acetic acic and gaseous constituents in experiments of deeper oxidation than this was ascribed to the reaction to shorten the carbon chain and was estimated by calculation. The method of calculation and the results are given in Table III. In

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[8] H. S. Mosher and C. F. Wurster, *J. Am. Chem. Soc.*, 77, 542 (1955).

TABLE III. RELATION BETWEEN THE AMOUNTS OF ACETIC ACID, DIBASIC ACID, CARBON DIOXIDE AND CARBON MONOXIDE FORMED, AND THE EXTENT OF OXIDATION REACTION

Experimental No.	DX-9	DX-7	DX-10	DX-8
Amount of *n*-decane reacted, g.	6.0	12.0	17.5	25.5
Extent of the reaction of *n*-decane, %	20.0	40.0	58.4	85.0
A. Amount of acetic acid produced, mmol.	35	70	122	238
B. Amount of carbon dioxide formed, mmol.	34	107	211	408
C. Amount of carbon monoxide formed, mmol.[a)]	5.5	13.9	26.4	48.7
D. Amount of dibasic acid produced, mmol.	18	19	32	59
Amount of acetic acid formed in the reaction to shorten the carbon chain, mmol. (A−D×35/18)	0	33	64	123
Amount of carbon dioxide formed in the reaction to shorten the carbon chain, mmol. (B−D×34/18)	0	71	151	296
Amount of carbon monoxide formed in the reaction to shorten the carbon chain, mmol. (C−D×5.5/18)	0	8.1	16.6	33.8

a) Sum of carbon dioxide+formic acid

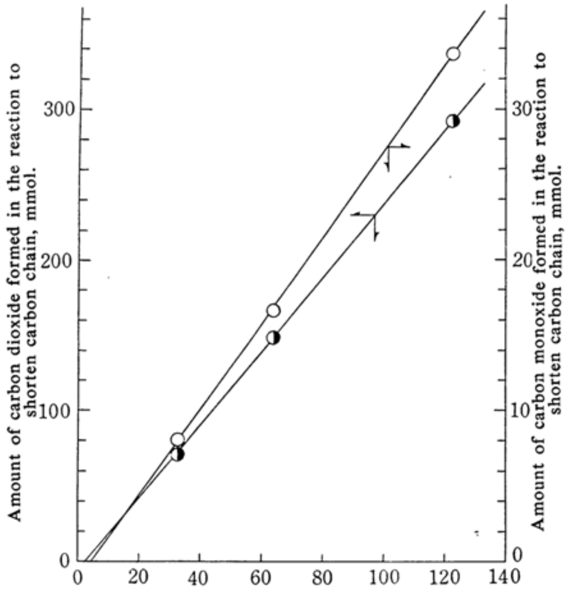

Fig. 5. Formation of acetic acid, carbon dioxide and carbon monoxide in reaction to shorten carbon chain.

the calculations of Table III, formic acid appearing in water-soluble products was regarded as a precursor to carbon dioxide and was so added to the latter.

The amounts of carbon dioxide and carbon monoxide which are thought to have been formed in the reaction to shorten the carbon chain were plotted respectively against the amount of acetic acid, resulting in straight lines, as is shown in Fig. 5. Thus, it is probable that Reactions A and B proceed together, as was presumed afore, and, at least in the reaction of carbon chain shortening, acetic acid and carbon dioxide, together with carbon monoxide, would be formed concurrently.

Ingredients in the Oil Layer.—The oil layer obtained after oxidation constitutes mainly of unchanged *n*-decane, but it also contains a small number of products from shallow oxidation (C_{10} ketone and C_{10} alcohol) and a minute amount of lower fatty acid. These products are estimated, to be from the amount of oxygen absorbed, negligible as compared with products from deep oxidation (water-soluble constituent and gaseous constituent); as no quantitative analysis was conducted, the composition was only roughly examined.

Ten grams of the oil layer from the experiment DX-7 in Table II (carbonyl content, 14.8% as C_{10} ketone, carboxyl content, 15.0% as C_{10} acid) were washed with dilute alkali and water. This sample was applied to the gas chromatography, in a method which has been reported previously[7)], and also to the chemical analysis. The results are given in Table IV.

In view of the range of relative retention time,

TABLE IV. COMPOSITION OF OILY MATERIAL

Ingredient	Gas chromatography		Chemical analysis
n-Decane	79.2		
n-Decanone-2	3.3	10.6	10.7
n-Decanone-3	2.1		
n-Decanone-4 *n*-Decanone-5	5.2		
Others (C_2-C_4 monobasic acid $+C_{10}$ alcohol)	10.2		
	100		

the fraction of C_{10} alcohol seems to be a mixture of isomers having the functional group at different positions, like the *n*-decanone fraction, but the amount was so small that characterization of the constituents was impossible.

On the other hand, the oil layer obtained in the series of experiments in Table II was directly analyzed chemically; the carbonyl content estimated as C_{10} ketone was 9.1% (DX-9), 14.3% (DX-7), 11.4% (DX-10) and 2.8% (DX-8), in the order of degree of oxidation. They were usually about 10% except for the last experiment of the deepest oxidation (the consumption of *n*-decane was 85.6% in DX-8). On the basis of these results, this oxidation reaction is thought to take a course through HPO to ketone and alcohol as the primary process in the same manner as in the oxidation of the system without water; moreover, the composition of the ketone (*n*-decanone) regarded as an intermediate is also identical with that in the thermal auto-oxidation of the system without water. Therefore, the course of this oxidation is thought to be that, initially, *n*-decanone (or *n*-decanol) is formed from *n*-decane, and that it is then subjected continuously to successive oxidation, without accumulating in the oil layer, to give acidic constituents and is then transferred into the aqueous layer.

Oxidation of Solid Paraffin.—Solid paraffin was oxidized in the same way as *n*-decane. The oxygen absorption curve, an example of which is shown in Fig. 2, assumes a straight line after a certain induction period, as does *n*-decane. The experimental results obtained at 150 and 160°C are tabulated in Table V, and an example of an experiment, in which oxidation was continued until the unchanged oil layer disappeared completely at a reaction temperature of 160°C, is presented in Table VI.

In Tables V and VI are shown analytical values for all the acidic ingredients in the aqueous layer, which was treated according to the after-treatment precedure illustrated for *n*-decane in Fig. 1. The unchanged oil layer and the aqueous layer were both distilled, and the residual fraction (b. p. 160°C<) of the latter was esterified in the same way as in Fig. 1. The residue (about $0.3\sim0.5$ g.) remaining after vacuum distillation of esters was not examined in further detail.

As for acidic ingredients, C_1—C_9 monobasic acids and C_4—C_9 dibasic acids were found over the whole range of oxidation, as in the case for *n*-decane. In gas chromatograms of samples GC-2 and GC-3 obtained by the method of treatment in Fig. 1, no peak corresponding to an unidentified substance was found in the range of a lower fraction than that of C_9 monobasic acid, and capric acid could not be detected, even by careful examination while changing the operating conditions for chromatography.

TABLE V. OYIDATION OF SOLID PARAFFIN

Experimental No.	DX-14		DX-17	
Solid paraffin charged, g.	15		20	
Amount of water charged, g.	85		80	
Reaction temp., °C	150		160	
Total reaction press., kg./cm^2	$18\sim60$		$17\sim80$	
Reaction time., hr.	9.8		8.3	
ρ_{max}, kg. cm^{-2} hr^{-1}	7.1		9.2	
θ, hr.	2.4		0.6	
Amount of oxygen absorbed, g.	19.0		29.7	
Solid paraffin consumed, g.	13.0		18.5	
Products in the aqueous layer				
	g.	wt. %	g.	wt. %
Formic acid	0.27	2.3	0.43	5.2
Acetic acid	3.76	32.5	7.26	37.7
Propionic acid	0.36	3.1	0.50	2.6
n-Butyric acid	0.24	2.1	0.88	4.6
n-Valeric acid	0.06	0.5	0.09	0.5
Caproic acid	0.08	0.7	0.21	1.1
Heptanoic acid	0.74	6.4	1.20	6.2
Caprylic acid	0.28	2.4	0.71	3.7
Pelargonic acid	0.22	1.0	1.13	5.9
Succinic acid	2.71	23.4	3.92	20.4
Glutaric acid	1.73	15.0	1.88	9.8
Adipic acid	0.63	5.4	0.59	3.1
Pimelic acid	0.23	2.0	0.23	1.2
Suberic acid	0.34	2.9	0.19	1.0
Azelaic acid	0.02	0.2	trace	—
Total	11.57	100.0	19.22	100.0
Gaseous products				
CO_2	7.52 g.		12.1 g.	
CO	0.54 g.		1.0 g.	
C=C	0		0.02 g.	
Others	0.49 l.		0.55 l.	

The effect of the reaction temperature on the product distribution can be seen in Table V. A better yield of dibasic acids and a higher ratio of glutaric acid against succinic acid are obtained at a lower temperature, while the amount of acetic acid produced is greater at a higher temperature, gaseous constituents such as carbon dioxide and carbon monoxide show similar tendencies.

The experiment of complete oxidation of the oil layer (cited as DX-20 in Table VI) was practised as follows: 1.3 g. of the oil layer recovered in the two experiments DX-18 and DX-19 and 18.2 g. of the viscous oily

TABLE VI. OXIDATION OF SOLID PARAFFIN

Experimental No.	DX-18	DX-19	DX-20
Amount of solid paraffin charged, g.	20	20	Recovered oil of DX-18, DX-19
Amount of water charged, g.	80	80	80.5
Reaction temp., °C	160	160	160
Total reaction, press., kg./cm^2	18~80	20~80	35~70
Reaction time, hr.	9.5	11.3	5.6
ρ_{max}, kg. cm^{-2} hr^{-1}	8.5	9.0	
θ, hr.	0.62	0.80	
Amount of oxygen absorbed, g.	31.7	30.4	
Amount of solid paraffin consumed, g.	18.0	18.5	

Products in aqueous layer

	g.	wt. %
Formic acid	3.39	9.6
Acetic acid	17.08	48.4
Propionic acid	1.54	4.4
n-Butyric acid	0.70	2.0
n-Valeric acid	0.20	0.6
Caproic acid	0.13	0.40
Heptanoic acid	0.64	1.8
Caprylic acid	0.18	0.5
Pelargonic acid	0.24	0.70
Succinic acid	7.72	21.8
Glutaric acid	2.67	7.6
Adipic acid	0.42	1.2
Pimelic acid	0.08	0.2
Suberic acid	0.01	0.3
Azelaic acid	trace	—
Sebacic acid	0.15	0.4
Higher acid not yet identified	0.05	0.1
Total	35.20	100.0

Gaseous products

CO_2	34.6 g.
CO	2.8 g.
C=C	0
Others	1.39 l.

matter obtained in the treatment of the aqueous layer (of Fig. 1) were joined together and oxidized in experiment DX-20 until the oil layer had completely disappeared. The results reveal that it is possible to convert starting hydrocarbons almost completely into water-soluble products. By comparing these results with those of experiment DX-17, it can be realized that perfectly deep oxidation converts monobasic acids to acetic acid, and dibasic acids to succinic acid. This finding agrees well with that of *n*-decane illustrated in Table II.

In order to compare the results for solid paraffin with those for *n*-decane, Table VII presents the amount of each acidic constituent produced per 1 kg. of hydrocarbon consumed in experiments of roughly the same depth of oxidation (extent of reaction: 85~92%). In summary, the yield of dibasic acids against consumed hydrocarbon is 29% for *n*-decane, poorer than the value of 40% for solid paraffin.

TABLE VII. AMOUNT OF DIBASIC ACID FORMED PER 1 kg. HYDROCARBON CONSUMED

Experimental No.	DX-8	DX-14	DX-17
Original hydrocarbon	*n*-Decane	Solid paraffin	Solid paraffin
Extent of reaction, %	85.1	86.6	92.5
Reaction temp., °C	160	150	160
Dibasic acid			
Succinic acid	215	209	212
Glutaric acid	66	133	102
Adipic acid	10	48	32
Pimelic acid	1	18	12
Suberic acid	1	26	10
Azelaic acid	0	2	0
Total	293	436	368
Monobasic acid			
Acetic acid	560	239	393
C_1, C_3—C_9 acid	283	216	288
Total	843	455	671

The amount of such lower fatty acids as acetic acid and propionic acid is large in the case of *n*-decane, but small, in the case of solid paraffin. It may therefore be concluded that in the case of *n*-decane the yield of dibasic acids is small, while that of lower monobasic acids is large. The discrepancy is probably due to the difference in the carbon chain length of the original hydrocarbons. It seems probable that *n*-decane, owing to its comparatively short carbon chain, has an extremely poor chance to form two moles of dibasic acids of C_4—C_5 by the random attack of a molecular oxygen, but that it has a large possibility to form one mole of dibasic acid and residual fragments of carbon chain, which will then turn into lower monobasic acids. On the contrary, in the case of solid paraffin composed mainly of *n*-paraffins of mean carbon number 26—27, no such restriction is imposed since its yield in dibasic acids is higher.

Comparison with Reactions in the Absence of Water.—In comparing the present oxidation reaction with the reaction without water added in advance[9], some consideration must be given

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[9] Hereafter we shall call this system the "anhydrous system". A small amount of water is certainly produced in the oxidation reaction, but it is usually carried away from the system together with exhaust gas, by virtue of some suitable apparatus in the works of Zellner[1], Buckmann[2] and Tsyskovskii[4]. Thus the system can be regarded as "anhydrous".

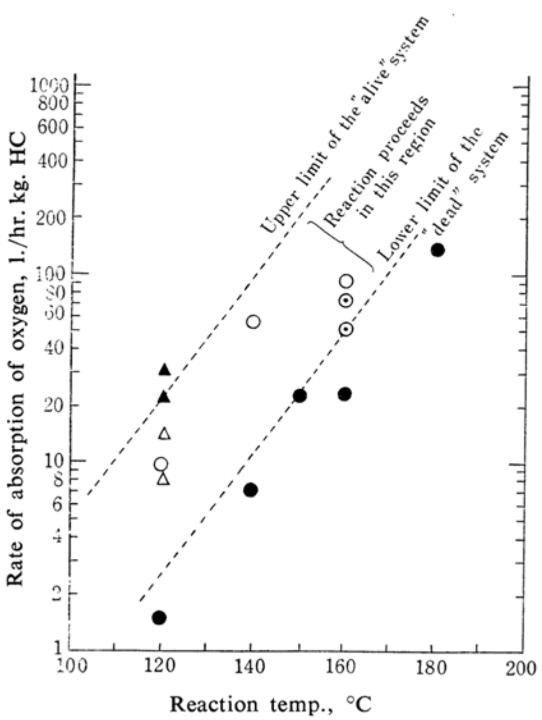

Fig. 6. Rate of oxygen absorption plotted against the reaction temperature.
▲ Instance of dead[2] △ Instance of alive[2]
● Instance of dead[9] ○ Instance of alive[9]
⊙ Instance of this experiment

to the characteristics of the present system, especially the role of water.

In the methods of both Zellner et al.[1] and Buckmann[2], solid paraffin in oxidized under strict control of the reaction temperature as well as of the amount of oxygen absorbed; too large[2] or too small[10] aeration is thought to inhibit the absorption of oxygen on account of the polymerization of reaction products.

For instance, Zellner assumed that the appropriate depth for the oxidation of products would correspond to a saponification value above 400[10], a recent patent has claimed a value of 600[3], and Buckmann considered it to be represented by an acid value above 490[2]; in every case, the main object of study was to realize a rapid and smooth arrival at this line before the reaction was retarded by these polymers. The relation between the reaction temperature and the rate of oxygen absorption observed in these studies, together with data from the present work, are shown in unified units in Fig. 6. (The rate of oxygen absorption is shown in liters of gas absorbed per 1 kg. of original hydrocarbon per hour and is denoted as l./hr. kg. HC). In our experiments, the rates of the oxygen absorption calculated are 56.1 and 78.3 l./hr. kg. HC respectively for DX-8 in Table II (the *n*-decane charged was 30 g., reaction temperature, 160°C; $\rho_{\max}$, 9.1 kg. $\mathrm{cm}^{-2}\,\mathrm{hr}^{-1}$) and for DX-17 in Table V (the solid paraffin charged was 20 g.; reaction temp., 160°C; $\rho_{\max}$, 9.2 kg. $\mathrm{cm}^{-2}\,\mathrm{hr}^{-1}$).

Zellner[10] called a state a "dead system" in which oxidation has been interrupted during the reaction and in which the replenishment of oxygen through aeration does not provoke further oxidation. Figure 6 gives examples of "alive" and "dead" reaction systems. In regions above and below the two dotted lines in the figure, the progress of reaction is stopped owing to the formation of polymers and other retarders.

In 1960 Tsyskovskii et al.[4], improving on the method of Zellner and Lister, oxidized *n*-paraffin with a b. p. of 240~350°C, a by-product of diesel fuel, with oxygen using manganese naphthenate as a catalyst at 135~155°C under ordinary pressure; the reaction product was then hydrolyzed at 160°C under about 15 atm., giving dibasic acids in an yield of 40% against the starting material. The composition of these dibasic acids, including succinic acid through sebacic acid, is almost identical with our results for solid paraffin listed in Table V. The reaction mechanism of hydrolysis at a high temperature in their method has not yet been elucidated, but it seems probable that hydrolysis[11] of a lactone-type compound at a high temperature and pressure was applied to the case of the recovery of fatty acids from oxidized oil.

When the present results of oxidation in systems containing water are compared with the data of previous literature, our method interestingly produces almost no polymers in spite of the small rate of oxidation. Namely, as may be seen from Fig. 6, the rate of oxygen absorption in this experiment lies in the region of "death", if the system were anhydrous, where reaction should cease owing to the formation of polymers. The reason why the reaction is not interrupted in the present system may be attributable to the inhibition of polymerization due to the ring rupture by water (hydrolysis) of lactonic substances during the reaction.

Examinations of the reaction velocity and the distribution of products in comparison with those in the anhydrous system[6] have been perfomed; they are tabulated in Tables VIII-1, 2 and 3,

In these tables are listed, for the sake of comparison, the results of oxidation at the same depth (1 mol. oxygen absorbed per 1

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[10] C. N. Zellner, U. S. Pat. 2486454 (1949).

[11] P. A. Moshkin, U. S. S. R. Pat. 116947 (1959); *Chem. Abstr.*, 53, 17541 (1959).

TABLE VIII-1. OXIDATION IN THE SYSTEM CONTAINING WATER AND THE ANHYDROUS SYSTEM

Exp. No.	Method of oxidation	Sample for oxidation, g.	Amount of water added, g.	Reaction temp., °C	$\rho_{\max}$ l./hr. kg. HC	θ, hr.
DX-9	This experiment	*n*-Decane 30	70	160	51.6	0.95
DX-16	Oxidation under ordinary pressure	*n*-Decane 50	0	160	174.2	0.73
DX-12	Same as above	*n*-Decane 50	0	160	78.4	2.20

TABLE VIII-2. OXIDATION IN THE SYSTEM CONTAINING WATER AND THE ANHYDROUS SYSTEM

Exp. No.	System	Depth of oxidation[a)] mol./mol.	Extent of reaction of *n*-decane[b)], %	Amount of gas formed, ml.			C_{10} Ketone C_{10} Alcohol g.	Water g.
				CO_2	CO	C=C		
DX-9	Containing water	0.99	20.0	2436	406	0	About 6	—
EX-16	Anhydrous	1.00	42.8	814	680	14	12.1	15.2
EX-12	Anhydrous	0.97	38.4	800	294	0	14.0	10.8

a) O_2 mol. absorbed per 1 mol. *n*-decane

b) (Amount charged − Amount recovered)) ÷ Amount charged × 100

TABLE VIII-3. OXIDATION IN THE SYSTEM CONTAINING WATER AND THE ANHYDROUS SYSTEM

Exp. No.	Monobasic acid, g.										Dibasic acid g.	Others g.
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_4—C_{10}	
DX-9	0.1	7.0	3.4	1.8	0.7	2.0	3.4	2.0	1.3	0	7.4	ca. 0.3
EX-16	1.0	3.8	3.6	3.0	2.6	2.4	2.0	1.2	trace	0.2	0	7.0
EX-12	1.0	4.0	2.4	3.2	3.6	3.4	2.2	1.0	0.2	0.4	0	10.8

mol. decane) in systems both with and without water. The rate of maximum oxygen absorption, $\rho_{\max}$, is shown with a calculated value per 1 kg. of decane in the same way as in Fig. 6, and the amounts of gas produced, C_{10} ketone + C_{10} alcohol and water, and other data listed in Table VIII-3 are all given in terms of weight calculated on the basis of 100 g. of *n*-decane charged. "Other" cited in Table VIII-3 means polymers other than dibasic acids in DX-9, and the sum of lower neutral compounds containing oxygen in EX-16 and EX-12.

As to the effect of water on the reactivity of *n*-decane, a comparison between the data from experiments DX-9 and EX-16 shown in Table VIII-1 indicates that, in the presence of water, the induction period, θ, increases a little, while the maximum rate of oxygen absorption, $\rho_{\max}$, is diminished to about one-third of that in the anhydrous system. That is to say, oxidation is greatly retarded by the addition of water.

As is shown in Table VIII-2, the extent of reaction is equal in these experiments on the basis of the oxygen absorbed, but the extent differs appreciably from experiment to experiment in terms of the *n*-decane consumed; the *n*-decane consumption is twice as much in the anhydrous system as that in water-containing system. Furthermore, the product distribution is also greatly different in these two reaction systems. In the system containing water, the amounts of the fractions of C_{10} ketone and C_{10} alcohol, which are regarded as primary intermediate products in the oxidation, are small, while the amount of acetic acid formed is large. In the case of the anhydrous system, no dibasic acids fraction comes out, whereas oxygen-containing neutral products of a low boiling point (shown as "others" in Table VIII-3) are abundant. Besides, it is interesting to note that caprylic acid is not formed in the system containing water. Monobasic acids of the C_3—C_7 range are continuously richly present in anhydrous systems, while in systems containing water C_3 acid and C_7 are richly present, but C_5 shows only a minimum.

As for gaseous products, carbon dioxide is richly present in the system containing water, while there is far less carbon monoxide than in the anhydrous system.

Thus, the product distribution shown in Tables VIII-2 and VIII-3 suggests that the following two reactions:

$$n\text{-decane} \rightarrow \text{HPO} \rightarrow C_{10}\text{ ketone, } C_{10}\text{ alcohol}$$

$$C_{10}\text{ ketone, } C_{10}\text{ alcohol} \rightarrow \text{succeeding oxidation products}$$

proceed with nearly the same velocity in the anhydrous system, whereas in the system containing water, the rate of the succeeding oxidation is so extremely that the C_{10} neutral fraction of intermediate products (ketone, alcohol) seems not to accumulate in the reaction system.

A comparison of both reactions has also been made from the standpoint of the dependency of the reaction velocity, $-d[O_2]/dt$, on the oxygen pressure. In the system containing water, ρ_{max} becomes independent of the partial pressure of oxygen above $P_{O_2}=6$ kg./cm², as has already been shown in Table I, while in the anhydrous system it becomes independent even under ordinary pressure at the same temperature (160°C). The mechanism of this oxidation (including the oxidation of *n*-decane or that of the succeeding C_{10} neutral fractions) seems substantially analogous to the reaction type proposed by Bolland-Gee[12]; hence, the reaction rate may be represented by the well-known equation, (1)[12], where R_i is the rate of chain initiation. The propagation steps are expressed by $R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot$, $RO_2\cdot + RH \xrightarrow{k_3} RO_2H + R\cdot$, and the termination by $2R\cdot \xrightarrow{k_4}$, $R\cdot + RO_2\cdot \xrightarrow{k_5}$, $2RO_2\cdot \xrightarrow{k_6}$, where $k_5^2 = k_4 k_6$.

$$-d[O_2]/dt = R_i^{1/2}\left(\frac{k_3}{k_6^{1/2}}\right)[RH] \times \left\{\frac{k_2/k_6^{1/2}[O_2]}{k_3/k_4^{1/2}[RH]+k_2/k_6^{1/2}[O_2]}\right\} \tag{1}$$

Assuming that in Eq. 1 the critical values of oxygen pressure, above which the value within the large bracket could be approximated to 1, are $[O_2]=6$ kg./cm² (in the system containing water) and $[O_2]=1$ kg./cm² (in the anhydrous system), as has been described before, the values of the ratio in the denominator $k_3/k_4^{1/2}$: $k_2/k_6^{1/2}$ are surmised to be fairly different between the two systems.

As the value of [RH] seems equal in both systems, the condition of the oxygen pressure independency can be expressed approximately by Eq. 2, where A_n, B_n (anhydrous system) and A_h, B_h (system containing water) represent $k_2/k_6^{1/2}$ and $k_3/k_4^{1/2}$ respectively.

$$\frac{A_n[1]}{B_n+A_n[1]} = \frac{A_h[6]}{B_h+A_h[6]} = 1 \tag{2}$$

In the system containing water, the condition $k_2\ [R\cdot] \gg k_3[ROO\cdot]$, which makes the content in large bracket 1, can not be established at O_2 pressure below 6 kg./cm²; that is to say, the applicability of Eq. 1 has been enlarged, namely into the region where ρ_{max} depends upon the oxygen pressure, since the reactivity of RH with molecular oxygen is enhanced as compared with that in anhydrous systems. If RH is presumed to be a C_{10} neutral substance produced during reaction, it is highly probable that these neutral ingredients are attacked preferentially by oxygen to form dibasic acids in the system containing water.

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[12] J. L. Bolland, *Proc. Roy. Soc.*, **A186**, 218 (1946).