which are typical of reaction between CO and  $H_2$  both for heterogeneous and metal-complex catalysts. In this connection a detailed study of reaction mechanisms catalyzed by transition-metal complexes may prove useful for devising new and improving traditional heterogeneous catalysts.

#### CONCLUSIONS

1. The effect has been found of the characteristics of each component of the catalytic system  $M_n L_m - AlX_3$ -reducing agent on its properties in the synthesis of alkanes from CO and  $H_2$ .

2. It was found by infrared spectroscopy that during the reaction a rhodium cluster is broken down to monocyclic.

3. A mechanism of the process including the cyclic transition state was proposed.

# LITERATURE CITED

- 1. G. C. Demitras and E. L. Muetterties, J. Am. Chem. Soc., <u>99</u>, 2796 (1977).
- 2. A. L. Lapidus and M. M. Savel'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 1470 (1978).
- 3. A. L. Lapidus and M. M. Savel'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 335 (1980).
- 4. M. M. Vannice, J. Catal., 37, 462 (1975).
- 5. J. R. Moss and W. A. G. Graham, J. Organomet. Chem., 18, P24 (1969).
- 6. B. F. G. Johnson, J. Lewis, and P. W. Robinson, J. Chem. Soc., A 1100 (1970).
- R. Colton, R. H. Farthing, and J. E. Knapp, Austral. J. Chem., <u>23</u>, 1351 (1970), D. Forster, Inorg. Chem., 8, 2556 (1969).
- 8. E. C. Ashby and J. Prather, J. Am. Chem. Soc., 88, 729 (1966).
- 9. U. S. Patent No. 2992248 (1961); C.A., 56, 167e (1962).
- 10. G. Becker, Introduction to the Electronic Theory of Organic Reactions [Russian translation], Mir, Moscow (1977).
- 11. C. P. Casey, M. A. Andrews, and D. R. McAlister, J. Am. Chem. Soc., <u>101</u>, 3371 (1979).
- S. B. Butts, E. M. Holt, S. H. Strauss, N. W. Alcock, R. E. Stimson, and D. F. Shriver, J. Am. Chem. Soc., <u>101</u>, 5864 (1979).
- 13. D. F. Shriver, J. Organomet. Chem., 94, 259 (1975).

and G. I. Nikishin

- 14. C. Masters, C. Woude, and J. A. Doorn, J. Am. Chem. Soc., <u>101</u>, 1633 (1979).
- 15. A. K. Smith and J. M. Basset, J. Mol. Catal., <u>2</u>, 229 (1977).
- 16. M. Ichikawa, J. Chem. Soc. Chem. Commun., 566 (1978).

CATALYTIC α-ALKYLATION OF ALDEHYDES WITH OLEFINS M. G. Vinogradov, I. P. Kovalev,

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The use of the one-electron oxidizing agent Mn (III) acetate in a stoichiometric quantity enables the  $\alpha$ -alkylation of aldehydes to be accomplished in acetic acid solution at 40-60°C. The yield of  $\alpha$ -alkyl-substituted aldehydes is 30-35% [1].

The purpose of the present study is to develop a catalytic method for the  $\alpha$ -alkylation of aldehydes by olefins in the presence of O<sub>2</sub> [2, 3], using as example the reaction between PrCHO and 1-heptene



Reaction (1) was carried out at 50-70° in AcOH containing acetates of the transition metals (Co, Mn, Ni, Ce, Cr) with bubbling of air through the mixture of reactants. During the reaction, PrCHO and 2-ethylnonanal are par-

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TABLE 1. Catalytic Alkylation of PrCHO with 1-Heptene<sup>a</sup>

Expt.	Catalyst	Conver- sion of 1-heptene %	2-ethyl- nonanal du	2-ethyl- nonanoic acid acid	4-unde- canone oito	pelargon- ic acid	icts, mole %	$s_{lpha}$	Total yield of products on con- verted 1-hep- tene, $\frac{1}{7}$
1 2 3 4 5 6 7 8 9 10	$\begin{array}{c} Co\left(OAc\right)_2 \\ Co\left(OAc\right)_2 \\ Co\left(OAc\right)_2 \\ Co\left(OAc\right)_2 \\ Co\left(OAc\right)_2 \\ f \\ Co\left(OAc\right)_2 \\ f \\ Co\left(OAc\right)_2 \\ Mn\left(OAc\right)_2 \\ Ni\left(OAc\right)_2 \\ Ce\left(OAc\right)_3 \\ Cr\left(OAc\right)_3 \end{array}$	83 35 92 77 60 60 53 70 88 88 86	$72 \\ 70 \\ 7 \\ 59 \\ 66 \\ 48 \\ 46 \\ 46 \\ 27 \\ 12$	14 10 63 23 12 14 18 8 18 18	8 9 5 10 14 23 25 34 43 51	4 9 15  4 7 1 4 8	2 2 10 8 4 11 4 11 8 11	90 (100) °C 90 93 89 85 73 (81) °C 72 64 (86) °C 51 35	56 83 66 61 61 70 93 85 85 84 100

<sup>a</sup>Solvent - AcOH, [PrCHO] = 4, [1-heptene] = 0.4, [catalyst] = 0.04 M (under the conditions mentioned the valency state of the catalyst corresponds to that given in the table); the rate of bubbling air was  $28 h^{-1}$ , 70°, 5 h. <sup>b</sup>The extent to which PrCHO is oxidized to PrCOOH is 5-15%. <sup>c</sup>In presence of a cocatalyst [Cu(OAc)<sub>2</sub>] =  $3 \times 10^{-4}$  M. <sup>d</sup>Air feed rate 7 h<sup>-1</sup>.

<sup>e</sup>Oxygen was bubbled through the reaction mixture at a rate of 14 h<sup>-1</sup>. f<sub>Solvent</sub> - PrCOOH. <sup>g</sup>Solvent - dimethylformamide (DMFA).

tially oxidized to the corresponding organic acids. Besides alkylation at the  $\alpha$ -carbon atom, PrCHO is alkylated at the carbonyl carbon atom with formation of 4-undecanone [4]



The alkylation products also contain a certain quantity of n-decane and pelargonic acid (Table 1). n-Decane is produced probably as a result of decarbonylation of 2-ethylnonanal as well as by the addition to 1-heptene of n-propyl radicals which occur during the decomposition of  $Pr\dot{C} = O$  radicals. Pelargonic acid is the alkylation product of the solvent AcOH with 1-heptene.

Since reactions (1) and (2) are competitive, it is convenient to represent the percentage contribution of reaction (1) to the total alkylation process by the quantity  $S_{\alpha}$  (the selectivity of  $\alpha$ -alkylation) determined from the equation\*

$$S_{\alpha} = \frac{[2-\text{ethylnonanal}] + [2-\text{ethylnonanoic acid}]}{[2-\text{ethylnonanal}[ + [2-\text{ethylnonanoic acid}] + [4-\text{undecanone}]}$$

The quantity  $S_{\alpha}$  is essentially dependent on the characteristics of the catalyst. The most active is the Co catalyst. Like the acetates of the other metals (see Table 1), it effectively catalyzes reaction (1) only at high concentrations, such as  $10^{-2}-10^{-1}$  M (Fig. 1, curve 1), while with low concentrations alkylation according to arrangement (2) predominates.

The selectivity of  $\alpha$ -alkylation increases in the presence of a cocatalyst – Cu(II) acetate, which is most efficient at a concentration of  $1 \times 10^{-5}$ -5  $\times 10^{-5}$  M. In the presence of the catalyst system Co(OAc)<sub>2</sub>/Cu(OAc)<sub>2</sub> (100:1) alkylation proceeds exclusively on the  $\alpha$ -carbon atom of the aldehyde. Addition of alkali-metal (Na, K, Li) acetates has no effect on S<sub> $\alpha$ </sub>.

In the course of the reaction, depending on the air supply rate and temperature, the catalyst can be in a different valence state. This is very typical of Mn and Co. In its turn the valence state of the metal considerably effects the composition of the alkylation products. For example, at 70° (see Table 1, Expt. 1) in the presence of Co (OAc)<sub>2</sub> (the solution is pink)  $S_{\alpha} = 90\%$ , but at 50°, when Co (II) is partly converted to Co (III) (green coloration),  $S_{\alpha}$  is reduced to 72%. The opposite picture is observed in the case of a manganese catalyst: when we

\* Because the n-decane content in the alkylation products is not very large (5-10%) and little dependent on the reaction conditions, it is not taken into consideration when  $S_{\alpha}$  is determined.

Aldehyde	Olefin	T., °C	Olefin conver- sion	α-Alkyl-substituted aldehyde	Yield on converted olefin, %
Acetic	1-Hexene	70	40	СНО	43
Propionic	1-Nonene	50	43	СНО	51
*	3,7-Dimethyl-7- hydroxy-1-octene	50	34	но	54
*	Dipentene	50	38	-СНО	62
Butyric	1-Heptene	70	35	CHO	55
*	3,7-Dimethyl-7- hydroxy-1- octene	70	51	но Сно	48
«	Dipentene	70	56		55
Isobutyric	1-Octene	70	25·	СНО	30
Valeric	1-Octene	70	46	CHO Pr	44

#### TABLE 2. Synthesis of $\alpha$ -Alkyl-Substituted Aldehydes

\* Solvent - AcOH, [aldehyde] = 4, [olefin] = 0.4,  $[Co(OAc)_2] = 4$  $\times 10^{-2}$ , [Cu (OAc)<sub>2</sub>] = 3  $\times 10^{-4}$  M, rate of bubbling air -10 h<sup>-1</sup>, 5 h.



Fig. 1. Relation between  $S_{\alpha}$  and Co (OAc)<sub>2</sub> concentration in reaction of PrCHO with 1-heptene using the redox systems Co (OAc)  $_{2}$ /O<sub>2</sub> (1), Co (OAc)  $_{2}$ /AcOOH (2), and Co (OAc)  $_{2}$ /PrCHO (3). The alkylation conditions are shown in the note in Table 3.

Fig. 2. Dependence of the stoichiometric coefficient x for Co (OAc)<sub>2</sub> in reaction with peracetic (1) and perbutyric (2) acids on the salt concentration. Solvent -AcOH,  $[Co(OAc)_2]/peracid = 4, 20^\circ$ .

change from  $M_n$  (OAc)<sub>2</sub> (an almost colorless solution at 70°) to  $M_n$  (OAc)<sub>3</sub> (a dark-brown solution at 50°) S<sub> $\alpha$ </sub> increases, on the other hand, from 73 (see Table 1, Expt. 4) to 96%. A drawback with the Mn (OAc)3 catalyst is the comparatively slow alkylation rate, two or three times lower than in the case of Co (OAc)<sub>2</sub>, as well as the formation of a large quantity of PrCOOH.

The best conditions for  $\alpha$ -alkylation found in the example of reaction (1) (Table 2) were used for the synthesis of other  $\alpha$ -alkyl-substituted aldehydes. As follows from Table 2, in the reaction under investigation, not only can 1-alkenes be used, but also dienes with isolated double bonds, such as dipentene, as well as functionally substituted olefins, for example, 3,7-dimethyl-7-hydroxy-1-octene. In the case of dipentene the reaction takes place selectively at the terminal multiple bond.

TABLE 3. Selectivity of  $\alpha$ -Alkylation (S $_{\alpha}$ , %) of PrCHO by 1-Heptene in the Presence of Various Redox Systems<sup>a</sup>

Redox system	(III) uM	Go (II)	Mn (II)	Ni (II)	Ce (III)	Gr (III)	Go (III)	W ithout catalyst
$M^{n}/O_{2}^{b}$ $M^{n}/AcOOH^{c}$ $M^{n+1}/aldehyde^{d}$	95 100 e	90 89 90	73 75 75	72 68 65	61  -	51 - 48	- 37e	35 36 37

a) Solvent – AcOH, [PrCHO] = 4 M, [1-heptene] = 0.4,  $[M^n (OAc)_n] = 4 \times 10^{-2} M$ , 70°,  $M^n$  – the valence indicated for the metal corresponds to its steady state in the course of the reaction.

b) Rate of supplying air -28 h<sup>-1</sup>.

c) The peracid was gradually added to the reactants mixture.

d)  $M^{n+1} = Mn (OAc)_3$  or  $Co (OAc)_3$ ,  $[M^{n+1}] = 1 \times 10^{-3} M$ .

e)  $S_{\alpha}$  was determined with  $[Mn(OAc)_3] = [Co(OAc)_3] = 4 \times 10^{-2} M$ and their low conversion (about 10%).



Fig. 3. Relation between stoichiometric coefficient x for Mn (OAc)<sub>2</sub> (1) and Ce (OAc)<sub>3</sub> (2) in reaction with peracetic acid. Solvent - AcOH,  $[M^{n}(OAc)_{n}]/[AcOOH] = 4, 20^{\circ}$ .

Fig. 4. Dependence of  $S_{\alpha}$  on temperature when the reaction of PrCHO with 1-heptene is initiated by the redox system Co(OAc)<sub>3</sub>/PrCHO in an inert atmosphere. Solvent - AcOH,  $[Co(OAc)_3] = 1 \times 10^{-3}$ ,  $[Co(OAc)_2] = 1.5 \times 10^{-2}$  M.

To find the role of the catalyst in the process under investigation, the  $\alpha$ -alkylation of PrCHO by 1-heptene has been studied in the presence of various redox systems:  $M^n/O_2$ ,  $M^n/AcOOH$ , and  $M^{n+1}/PrCHO$  (in an inert atmosphere). As follows from the tables the catalysts, according to their activity in reaction (1) expressed by the quantity  $S_{\alpha}$ , are placed in the same order for all the redox systems investigated (the valence relates to the state of the catalyst in the course of the reaction): Mn(III) > Co(II) > Mn(II) > Ce(III) > Cr(III) > Co(II).

The dependence of  $S_{\alpha}$  on the catalyst concentration (see Fig. 1) is of the same type (a pronounced increase in  $S_{\alpha}$  in the  $10^{-3}$ - $10^{-2}$  M catalyst concentration range), both in the presence of  $O_2$  (curve 1) and when employing the redox systems Co (OAc)<sub>2</sub>/AcOOH (curve 2) and Co (OAc)<sub>3</sub>/PrCHO (curve 3). The increase in  $S_{\alpha}$  with a rise in the catalyst concentration is apparently associated with a reduction in the contribution from the free-radical mechanism (2) in the alkylation. When  $M^n/RC$  (O)OOH redox systems are employed this can be judged, in particular from the variation of the stoichiometric coefficient (x) for Co (OAc)<sub>2</sub>, Mn (OAc)<sub>2</sub>, and Ce (OAC)<sub>3</sub> in the reaction of AcOOH with PrC (O)OOH (Figs. 2 and 3).

The reaction of peracids with metal salts was studied previously in [5-7], but data on the stoichiometry of this reaction is lacking. The stoichiometric coefficient x for the metals referred to in reaction with  $_{3}$  peracids varies from 1 to 2 (with excess of metal salt) in the range of salt concentrations between  $2 \times 10^{-3}$  and  $1 \times 10^{-2}$  M. With  $[M^{n}] \le 2 \times 10^{-3}$  M, when x = 1, decomposition of the peracid proceeds according to Eq. (3). The free radicals which arise ('OH) abstract hydrogen from PrCHO, initiating the free-radical reaction at Eq. (2)

$BC(0)OOH + M^n \rightarrow BC(0)OM^{n+1} + OH$	(3)
$M^{n}$ : OF $M^{n+1}OF$	(4)
$M + OH \rightarrow M$ OH	(5)
$2\mathbf{M}^{n} + \mathrm{RC}(0)\mathrm{OOH} \rightarrow \mathrm{RC}(0)\mathrm{OM}^{n+1} + \mathrm{M}^{n+1}\mathrm{OH}$	•

With  $[M^n] \ge 0.01$  M the coefficient x for  $M^n$  (OAc)<sub>n</sub> becomes equal to 2 in accordance with the overall equation (5). Under these conditions the reaction rate of 'OH radicals with the metal is considerably higher than that of their reaction with PrCHO. Thanks to reaction (4), with a high catalyst concentration inhibition of the free-radical ketone-formation process occurs [Eq. (2)]. It may also be assumed that with a high concentration the metal salt reacts with RC (O)OOH as a dimeric complex  $M_2(OAc)_4$ , i.e., reaction (5) is single-stage. Nevertheless, such a hypothesis is not valid, at least for Co (OAc)<sub>2</sub>, which was found in [8] to be present in an acetic acid solution as a mononuclear complex in the  $10^{-2}$ - $10^{-1}$  M concentration range.

Thus, with a low catalyst concentration  $\alpha$ -alkylation of aldehydes takes place by a free-radical mechanism as a result of addition of the RCHCHO radical to the olefin. Under these conditions low selectivity of  $\alpha$ -alkylation is observed (S<sub> $\alpha$ </sub> = 35-37%). This does not depend on the type of catalyst and agrees with the value obtained in the absence of a catalyst (Table 3). The preferential formation of the ketone in (2) under conditions of freeradical initiation is attributed to the high stability of the RC = O radical in RCHCHO.

With a high catalyst concentration alkylation probably takes place in the coordination sphere of the metal ion as indicated by the following facts: a) high  $\alpha$ -alkylation selectivity ( $S_{\alpha} = 95-100\%$ ); b) the same dependence of  $S_{\alpha}$  on the characteristics and concentration of the catalyst when different redox systems are used; c) the absence from the reaction mixture of acids with one carbon atom less than in the original aldehyde which would have been formed as a result of oxidation by the oxygen of the RCHCHO radical.

The individual stages of catalytic  $\alpha$ -alkylation can be shown by Eqs. (6)-(12).

0 0 0	(6)
$\mathbf{R} \xrightarrow{H} + \mathbf{M}^{n+1} \rightarrow \mathbf{R} \xrightarrow{H} \mathbf{M}^{n+1} \xrightarrow{-\mathbf{H}^+} \mathbf{R} \xrightarrow{H} \mathbf{M}^{n+1}$	
. (I)	
$(1) + \mathbf{R}' \xrightarrow{\sim} \mathbf{R} \xrightarrow{\mathbf{N}'} \mathbf{M}^{n+1} \leftarrow \begin{bmatrix} \mathbf{R}' \\ \mathbf{M} \end{bmatrix} \xrightarrow{\sim} \mathbf{R}'$	
$\begin{bmatrix} H \\ H \\ H \end{bmatrix} = 0$	(7)
$\rightarrow \left  \begin{array}{c} \mathbf{R} \\ \mathbf{M}^{n+1} \\ \mathbf{R}' \end{array} \right  \rightarrow \mathbf{R}' \qquad \mathbf{H} \qquad \mathbf{H}^{n}$	(1)

$$(III) + R \xrightarrow{H} R \xrightarrow{H} H + R \xrightarrow{O} (8)$$

$$(I) \rightleftharpoons R \stackrel{\circ}{\longrightarrow} R \stackrel{\circ}{\longrightarrow} R \stackrel{\circ}{\longrightarrow} H \stackrel{\circ}{\longrightarrow} H \stackrel{\circ}{\longrightarrow} H^{n}$$
(9)

$$(IV) + R \bigwedge_{H}^{O} \rightarrow R \bigwedge_{H}^{O} + R \bigwedge_{H}^{O}$$
(10)

$$R \xrightarrow{O} + M^{n}OAc \rightarrow \left[ R \xrightarrow{O} \\ M^{n}OAc \\ (V) \end{bmatrix} \rightarrow R \xrightarrow{O} \\ OAc + M^{n-1}$$
(11)

$$\mathbf{M}^{n}, \, \mathbf{M}^{n-1} \xrightarrow{O_{2}} \mathbf{M}^{n+1} \tag{12}$$

Since the acetates of the investigated metals are in the activated (oxidized) form  $(M^{n+1})$ , such as Co  $(OAc)_3$ and Mn  $(OAc)_3$  -low-spin complexes [9] with vacant d-orbitals, they are strong Lewis acids which cause deprotonation of the aldehyde forming the enolate (1), which reacts with the olefin according to Eq. (7). As in other homogeneous-catalytic reactions of similar type in [10], addition of the olefin evidently procedes its coordination on the central ion. Dissociation of the unstable  $\sigma$ -complex (I) gives the radical (II) which detaches hydrogen from the original aldehyde to form the  $\alpha$ -alkyl-substituted alkanal. Since 2-ethylnonanal, prepared by the alkylation of PrCHO with 1-heptene in AcOD, contains no deuterium, the heterolytic decomposition of complex (II) under the conditions chosen either does not occur or makes an insignificant contribution to catalytic alkylation. The addition to an olefin contrary to the Markovnikov principle permits the hypothesis that the  $\alpha$ -alkylation of aldehydes in the coordination sphere of a metal takes place preferentially according to a homolytic mechanism with the participation, accordingly, of an enolate of  $\alpha$ -alkyl complex.



The homolytic decomposition (9) of the enolate (I) to form the RCHCHO radical competes with reaction (7). This radical can not only add on to the olefin, but also interact with the aldehyde according to (10) to form acyl radicals. Therefore, the selectivity of the  $\alpha$ -alkylation depends on the ability of the metal ions to react with radicals (IV) [this reaction is the reverse of (9)], in this way displacing the equilibrium in (9) towards complex (I). The equilibrium in (9) shows that the enolate (I) can be regarded as a  $\sigma$ -complex of the radical in (IV) with the metal acetate in [11].

The ability of metal carboxylates to form a  $\sigma$ -complex (I) with radicals (IV) should be connected with the facility of substituting ligands on the metal ion. In fact, the order of activity found for the ions in the catalytic  $\alpha$ -alkylation of PrCHO (see Table 3) accords qualitatively with the order of lability of transition-metal complexes in a ligand exchange reaction d<sup>4</sup>, d<sup>5</sup> > d<sup>3</sup> > d<sup>6</sup> [12]. The existence of the equilibrium in (9) is confirmed by the dependence of the value of S<sub> $\alpha$ </sub> on the catalyst concentration (see Fig. 1) and the temperature (Fig. 4).

However, the linking of enolate radicals to complex (I) according to Eq. (9) does not fully account for the high selectivity of  $\alpha$ -alkylation, because the acyl radicals occurring according to Eqs. (8) and (10) are capable of addition to an olefin according to the arrangement in (2). It can only be assumed that the acyl radicals also form a labile  $\sigma$ -complex (V) with the catalyst which, unlike complexes (I) and (II), is decomposed according to the heterolytic mechanism in (11) [13,14]. Heterolysis of the C-M bond in complex (V) is facilitated by the formation of the stable acylium cation RC=O. Because Cu(II) ions are considerably more reactive in oxidizing free radicals than the ions of the other metals investigated [13] the use of Cu(II) as a cocatalyst leads to a marked increase in the selectivity of  $\alpha$ -alkylation.

## EXPERIMENTAL

The initial aldehydes and olefins were commercial reactants purified by distillation immediately before the experiment. Co (II), Mn (II), Ni (II), Ce (III), Cr (III), and Cu (II) acetates were purified by recrystallizing them twice from 80% AcOH. Co (III) [7] and Mn (III) [15] acetates were prepared according to well-known methods. Peracetic and perbutyric acids were prepared by the reaction of  $H_2O_2$  with acetic and butyric anhydrides respectively.

The PMR spectra were obtained in  $CCl_4$  in a "Varian-DA-60-IL" spectrometer (60 MHz). The IR spectra were obtained with a thin layer in a UR-20 instrument and the mass spectra in a "Varian-MAT CH-6" instrument. Gas -liquid chromatography was carried out in an LKhM-8MD (5) instrument with a flame-ionization detector in 300  $\times$  0.3 cm columns, 15% PFMS-4 on Chromosorb R and 10% PEG-20M + 1% terephthalic acid on Chromaton N-AW.

<u>Procedure for Catalytic  $\alpha$ -Alkylation of PrCHO with 1-Heptene.</u> A mixture of 100 g (1.4 mole) of PrCHO and 13.7 g (0.14 mole) of 1-heptene was placed in a cylindrical 200 × 50 mm-glass reaction vessel fitted with a porous glass partition and connected to a reflux condenser. To the mixture of aldehyde and olefin was added 0.5 g (0.014 mole) of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O and 0.02 g (1 × 10<sup>-4</sup> mole) of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O dissolved in 200 ml of AcOH. Air was bubbled through the resulting solution at the rate of 7 h<sup>-1</sup> for 6 h at 70°. The unreacted aldehyde and olefin were then distilled off and the mixture was treated with water, extracted with petroleum ether, and the extract distilled. We isolated 8.27 g of 2-ethylnonanal of 95-97% purity, bp 90-92° (10 mm). PMR spectrum ( $\delta$ , ppm): 9.49 d (CHO), J = 2.6 Hz. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1725 (C = O), 2705 (HCO).

The residue was treated with 40% NaOH solution, HCl was added till the reaction was acid, it was extracted with petroleum ether, and the extract distilled. The product was 1.82 g of 2-ethylnonanoic acid, bp120° (3mm).

PMR spectrum ( $\delta$ , ppm): 10.87 s (COOH). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1730 (C = O), 3540 (COH).

Other  $\alpha$ -alkyl-substituted aldehydes were prepared similarly.

 $\frac{2-\text{Methylundecanal, bp 132-134° (18 mm).}}{(\nu, \text{ cm}^{-1}): 1725 (C = O), 2705 (HCO).}$  PMR spectrum ( $\delta$ , ppm): 9.45 d (CHO), J = 2.6 Hz. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1725 (C = O), 2705 (HCO).

<u>2-Propyldecanal, bp 137-139° (17 mm).</u> PMR spectrum ( $\delta$ , ppm): 9.53d(CHO), J = 2.6 Hz. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1725 (C = O), 2705 (HCO).

<u>9-Hydroxy-2,5,9-trim ethyldecanal, bp106-108° (0.2 mm).</u> PMR spectrum ( $\delta$ , ppm): 3.65 s (OH), 9.49 d (CHO), J = 2.8 Hz. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1725 (C = O), 2710 (HCO), 3425 (OH).

 $\frac{2-\text{Ethyl-9-hydroxy-5,9-dimethyldecanal, bp 115-117^{\circ} (0.2 \text{ mm}).}{\text{d} (CHO), J = 2.8 \text{ Hz}. \text{ IR spectrum } (\nu, \text{cm}^{-1}): 1725 \text{ (C = O)}, 2710 \text{ (HCO)}, 3425 \text{ (OH)}.}$ 

 $\frac{2-\text{Methyl}-4-(4-\text{methylcyclohex}-3-\text{ene}-1-\text{yl})\text{pentanal, bp 103-105° (0.2 mm).}}{\text{m (CH = C), 9.45 d (CHO), J = 1.6 Hz. IR spectrum (<math>\nu$ , cm<sup>-1</sup>): 1725 (C = O), 2710 (HCO).}

 $\frac{2-\text{Ethyl}-4-(4-\text{methylcyclohex}-3-\text{ene}-1-\text{yl})\text{pentanal, bp }113-115^{\circ} (0.3 \text{ mm}).}{(\text{CH}=\text{C}), 9.45 \text{ d} (\text{CHO}), \text{J}=1.6 \text{ Hz}. \text{ IR spectrum } (\nu, \text{cm}^{-1}): 1725 \text{ (C}=\text{O}), 2710 \text{ (HCO)}.}$ 

 $\frac{2,2-\text{Dimethyldecanal, bp 68° (4 mm).}}{1728 (C = O), 2720 (HCO).}$  PMR spectrum ( $\delta$ , ppm): 9.55 s (CHO). IR spectrum ( $\nu$ , cm<sup>-1</sup>):

A study of the decomposition stoichiometry of peracids by Co (II), Mn (II), and Ce (III) acetates was carried out by cerimetric titration of Co (III), Mn (III), and Ce (IV), and with low concentrations of Mn (II) and Co (II) spectrophotometrically in a Specord UV-VIS instrument at  $\lambda$  620 nm for Co (III) and  $\lambda$  465 for Mn (III).

### CONCLUSIONS

1. The catalytic  $\alpha$ -alkylation of aldehydes by olefins has been accomplished in acetic acid containing acetates of transition metals of variable valence, in the presence of oxygen. Based on this reaction,  $\alpha$ -alkyl-substituted aldehydes of diverse structure have been synthesized in 30-60% yield on the olefin converted.

2. The selectivity of the  $\alpha$ -alkylation depends on the properties of the metal ion as well as its valence state in the course of the reaction. It diminishes in the order: Mn(III) > Co(II) > Mn(II) ~ Ni(II) > Ce(III) > Cr(III) > Co(III). A mechanism has been proposed for the catalytic  $\alpha$ -alkylation of aldehydes in which the key stage is the reaction between an enolate complex of the transition metal and the olefin.

## LITERATURE CITED

- 1. G. I. Nikishin, M. G. Vinogradov, and G. P. Il'ina, Zh. Org. Khim., 8, 1401 (1972).
- 2. M. G. Vinogradov, G. I. Nikishin, I. P. Kovalev, S. P. Verenchikov, V. S. Markevich, B. S. Strel'chik, and M. L. Gringol'ts, Inventor's Certificate No. 759501, Byull. Izobr., No. 32 (1980).
- 3. M. G. Vinogradov, G. I. Nikishin, S. P. Verenchikov, O. N. Petrenko, I. P. Kovalev, V. N. Pavlichev, V. N. Masyutin, V. S. Markevich, G. A. Stepanova, B. S. Strel'chik, and M. L. Gringol'ts, First Petrochemical Symposium of Socialist Countries, Summaries of Papers, Baku (1978), p. 129; Neftekhimiya, <u>19</u>, 809 (1979).
- 4. G. I. Nikishin, M. G. Vinogradov, and R. V. Kereselidze, Izv. Akad. Nauk SSSR, Ser. Khim., 1624 (1967).
- 5. C. E. H. Bawn and J. E. Jolley, Proc. Roy. Soc. A, London, 237, 297 (1956).
- 6. E. Boga, I. Kiricsi, A. Deer, and F. Marta, Acta Chim. Acad. Scient. Hung., 78, 89 (1973).
- 7. E. Koubek and J. O. Edwards, J. Inorg. Nucl. Chem., 25, 1401 (1963).
- 8. C. F. Hendriks, H. C. A. van Beek, and P. M. Heertjes, Ind. Eng. Chem. Prod. Res. Develop., 17, 260 (1978).
- 9. S. S. Lande, C. D. Falk, and J. K. Kochi, J. Inorg. Nucl. Chem., <u>33</u>, 4101 (1971).
- 10. G. Henrici-Olivé and S. Olivé Weinheim, Introduction to the Electronic Theory of Organic Reactions, Verlag Chemie (1977), New York, Monographs in Modern Chemistry, Vol. 9, ISBN 3527256865, S 161330002.
- 11. M. G. Vinogradov, S. P. Verenchikov, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., 982 (1972).
- 12. F. Basolo and R. G. Pearson, Mechanism of Inorganic Reactions, 2nd Ed. Wiley, New York-London (1967).
- 13. J. K. Kochi in: Free Radicals (ed. by J. K. Kochi), No. 1, 643, 668 (1973), Interscience, New York and London.
- 14. H. Elroi and D. J. Meyerstein, J. Am. Chem. Soc., 100, 5540 (1978).
- 15. G. Brauer (editor), Handbook of Preparative Inorganic Chemistry (1956). 2nd Ed., translated by R. F. Riley and P. G. Steele, Academic Press, New York-London (1963).