

## CONVERSION OF OLEFINS TO UNSATURATED CARBONYL COMPOUNDS

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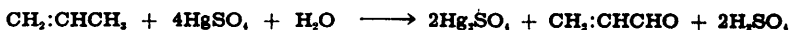
**PREVIOUS WORK.** The liquid-phase oxidation of olefins by mercury (II) salts to unsaturated aldehydes or ketones, first noted incidentally by Denigès (1), has since been reported only in patents. Thus Macallum (6) claimed the production of acrolein from propylene by oxidation with an aqueous reagent containing 3-24% mercury (II) sulfate and up to 15% (preferably 2-5%) sulfuric acid. Yields as high as 75% were obtained when calculated on the basis of mercury (II) sulfate consumed, but no yields based on propylene were given. For the same conversion Herstein (2) specified 16.7% HgSO<sub>4</sub> and 22% H<sub>2</sub>SO<sub>4</sub>, and used a series of steps comprising absorption of propylene at about 20°, stripping of uncombined propylene at 85-105°, digestion at the same temperature, and steam distillation of acrolein. Later Herstein (3) effected the absorption at 85-105° and removed acrolein as formed by a current of propylene. Yale and Hearne (8) found non-tertiary acyclic olefins having more than three carbon atoms to be converted into ketones by mercury (II) oxide suspended in 1-2% aqueous acid; RCH<sub>2</sub>CH:CH<sub>2</sub> gave RCOCH:CH<sub>2</sub>, and RCH:CHCH<sub>2</sub> gave RCOCH<sub>2</sub>CH<sub>2</sub> and RCH<sub>2</sub>COCH<sub>2</sub>, but not RCH:CHCHO.

**EXPERIMENTAL WORK.** Objectives of the present study were to test the patent claims referring to propylene, to extend the reaction to higher olefins, and to employ other cheaper oxidizing agents. The latter was tried first, without success. The following salt+acid combinations in various concentrations gave no acrolein upon attempted reaction with propylene: Copper (II) chloride in hydrochloric acid, with or without potassium chloride; copper (II) sulfate in sulfuric acid, with or without potassium sulfate or silver sulfate; iron (III) chloride in hydrochloric acid; iron (III) sulfate in sulfuric acid; and silver nitrate in nitric acid.

Among mercury (II) salts, the nitrate and the sulfate gave acrolein but the chloride, phosphate, and acetate did not. Even the nitrate when tried in 10% nitric acid produced no acrolein; evidently this sensitive aldehyde cannot exist long in such a concentration of nitric acid. Accordingly all further work was with HgSO<sub>4</sub>.

In most experiments to determine yields, measured volumes of propylene (Phillips 99%) were passed successively through a gas-washing bottle containing the oxidizing solution and a water scrubber to remove acrolein prematurely released (none was ever found) to a gas collector where the residual

volumes were measured. The aqueous oxidizing solution contained either 5% or 10% mercuric (II) sulfate and from 3% to 25% sulfuric acid. After about a liter of propylene had been passed through 170 ml of the solution, the latter was heated *in situ* to 90°C for an hour and blown with steam for a few minutes to remove the last unreacted propylene. The suspension of yellow mercury salt-olefin complex was transferred to a flask and exhaustively steam-distilled. Acrolein began to come over after 10-25 ml of distillate had been collected and usually continued until the distillate amounted to 1000-1500 ml. Distillation was continued until the distillate gave no appreciable turbidity with 2, 4-dinitrophenylhydrazine reagent. Evidently the formation of acrolein is a slow process, probably depending on hydrolysis of the complex. The carbonyl compounds in an aliquot volume of the steam distillate were determined by titration of the acid they liberated from aqueous hydroxylamine hydrochloride, bromphenol blue being used as indicator [cf. Maltby and Primavesi (7) ]. From the known amounts of propylene and mercuric sulfate consumed and the amount of acrolein produced, yields could be calculated from the equation



In two runs, propylene absorption was effected at other than room temperatures to test this variable, since the patents specify 20° (2), 50-60° (6) and 85° (3) as preferred.

Qualitative trials showed that isobutylene (made by pyrolysis of *t*-butyl alcohol over  $\text{Al}_2\text{O}_3$  at 400-500°) yields at least chiefly methacrolein (identified as the 2, 4-dinitrophenylhydrazone) by oxidation with mercury (11) sulfate. Since this reaction had not previously been reported, it was similarly studied at both concentrations (5% and 10%) of  $\text{HgSO}_4$  solution. One trial run with cyclohexene similarly showed 2-cyclohexen-1-one to be the product, and one quantitative treatment was carried out. Since the hydrocarbon is a liquid, 2 ml of it were added to the usual 170 ml of oxidizing reagent. The estimation of unreacted olefin was accomplished by measuring total unsaturated compounds with bromine (4) after reaction and deducting the amount of 2-cyclohexene-1-one shown by the hydroxylamine method.

**RESULTS AND DISCUSSION.** Results of quantitative runs with propylene and isobutylene are shown in Tables I and II. The one cyclohexene conversion, done with 5%  $\text{HgSO}_4$  + 10%  $\text{H}_2\text{SO}_4$ , initially at room temperature, gave a yield of 19% based on cyclohexene and 51% based on mercury (II) sulfate.

TABLE I

*Yields of Acrolein from 5%  $\text{HgSO}_4$  Solutions at Various Acidities and Absorption Temperatures.*

ABSORPTION TEMPERATURE °C	CONC. OF $\text{H}_2\text{SO}_4$ IN REAGENT %	ACTUAL YIELD DIVIDED BY THEORETICAL YIELD BASED ON	
		$\text{C}_3\text{H}_4$ %	$\text{Hg SO}_4$ %
25	3	12	29
25	5	15	35
25	10	24	58
25	15	28	80
25	20	25, 26	62, 63
25	25	7	18
0	10	24	53
60	10	22	63

TABLE II  
*Yields of Methacrolein at Various Acidities and Two Concentrations of HgSO<sub>4</sub> at 25°*

CONCENTRATION OF H <sub>2</sub> SO <sub>4</sub> , %	CONCENTRATION OF HgSO <sub>4</sub> , %	ACTUAL YIELD DIVIDED BY THEORETICAL YIELD BASED ON	
		C <sub>3</sub> H <sub>6</sub> , %	Hg SO <sub>4</sub> , %
1	5	0.2	1.5
5	5	13	22
10	5	16	16
15	5	12	13
20	5	9	11
2	10	4	3
5	10	5.5	7.7
10	10	12	8
15	10	7	6
20	10	"	5

Table I for propylene oxidation shows that (1) the optimum acidity is 15%, (2) absorption temperature has a negligible effect within the limits studied, (3) yields based on HgSO<sub>4</sub> can be made reasonably satisfactory, as claimed by Macallum, and (4) yields based on propylene are disastrously low. From Table II it may be further concluded that (2) 5% HgSO<sub>4</sub> is slightly more efficient than 10% HgSO<sub>4</sub>, (1) isobutylene is much more susceptible to side reactions or consecutive reactions than propylene, since yields are so much lower and, (3) the optimum acidity is lower for isobutylene than for propylene. Even though 2-cyclohexene-1-one, unlike the acroleins, cannot be oxidized further at the carbonyl group, the yield is disappointingly low.

While the low efficiency of conversion of hydrocarbons to carbonyl compounds, the high cost of mercury (II) sulfate, and the difficulty of regenerating it combine to render the process of little commercial promise, it is desirable to consider *why* the yields are so low. One possibility is that the olefin becomes hydrated instead of oxidized; propylene would thus produce isopropyl alcohol. To evaluate the seriousness of this side-reaction, isopropyl alcohol was determined in an aliquot of one of the typical distillates by chromic acid oxidation and acetone determination (5). The quantity of alcohol accounted for only an additional 1.7% of the propylene consumed. Another possible side-reaction is polymerization; but the distillates contained no appreciable amount of hydrocarbon oils extractable by ether. Since free mercury, as well as mercury (I) sulfate, always appeared in residues and steam distillates after reaction, destruction of products by oxidation was suspected. A trial at steam-distilling acrolein out of 5% HgSO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> confirmed this; no acrolein could be recovered. No means of avoiding this overoxidation, which may evidently be accomplished by even mercury (I) salts, has been devised, though sweeping out the product with excess olefin or an inert gas, as recommended by Herstein (3), should be of some help.

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