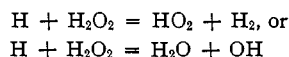


atom collides with oxygen inelastically, a second center of reaction is started. Hydroxyl, ozone, hydrogen peroxide, water, hydrogen atoms, etc., are again formed; in fact, the various so-called "chain reactions" take place in this second sphere of action as in the first. The high-speed hydrogen atoms from this second sphere will likewise penetrate, in random directions, the surrounding gas. Some atoms will advance in line with the original atom to carry the reaction forward. Others will dart backward to ignite unburned gas which may remain between the two spheres of reaction, or may even penetrate the first sphere which has since expanded, and there react with whatever may be available such as a hydrogen peroxide molecule, ozone, etc.

Suppose now that lead tetraethyl molecules be "stationed" throughout the hydrogen-oxygen mixture, and assume that they can act as effective barriers to the travel of the high speed hydrogen atoms. When an explosion is started hydrogen atoms are shot out of the zone of reaction, but a large percentage of them is captured by the intervening "screen" of lead tetraethyl molecules. Only relatively few escape to start the secondary reaction zones. Burning (explosion) is accordingly slower, and in consequence the violence (temperature and pressure) of the reaction is subdued. This explains the anti-knock effect observed.

In each reaction zone the usual "chain" reactions occur. The chief difference, however, is

that the hydrogen atom concentration would be lowered by the presence of the lead tetraethyl. Hence, reactions such as



would be less likely to occur and the net result would be an increase in the amount of hydrogen peroxide which could be recovered.

The above picture of the manner in which the explosion is propagated is in harmony with the various "chain reaction" theories. The latter are merely supplemented by the assumption that the hydrogen atom may have an exceptionally long free path. The further assumption is made that lead tetraethyl has a relatively high "absorption coefficient" for hydrogen atom. A direct determination of this coefficient for hydrogen atom, also for oxygen atom, and for free radicals from organic compounds could probably be made readily. Such data might assist in the development of a satisfactory explanation of anti-knock action of general application.

Summary

Lead tetraethyl added to electrolytic gas was found to increase the yield of hydrogen peroxide formed in an explosion at reduced pressure. A theory consistent with the anti-knock effect is presented in explanation of this result.

WILMINGTON, DEL.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Some Physical Constants of Methyl Ethyl Ketone and an Investigation of its Addition Compound with Sodium Iodide Dihydrate

BY W. A. FELSING, LOUISE SHOFNER AND N. B. GARLOCK

Introduction.—Lochte¹ studied some of the derivatives of methyl ethyl ketone and proposed for the purification of this substance the sodium iodide dihydrate addition compound scheme so successfully used for acetone by Shipsey and Werner.² Wadsworth and Dawson³ questioned the validity of Lochte's method, their contention being based upon a study of the system sodium iodide-methyl ethyl ketone. Since Lochte's method involved the system sodium

iodide-methyl ethyl ketone-water, it has seemed desirable to prepare pure methyl ethyl ketone by the two methods (bisulfite and sodium iodide dihydrate), to compare their vapor pressures, densities and indices of refraction, and to determine the composition of the solid product formed when sodium iodide dihydrate reacts with methyl ethyl ketone.

Methods and Apparatus.—The *vapor pressures* were determined by the static method used and described by Felsing and Thomas,⁴ all the usual precautions for high accuracy being observed.

(1) Lochte, *Ind. Eng. Chem.*, **16**, 956 (1924).

(2) Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

(3) Wadsworth and Dawson, *ibid.*, 2784 (1926).

(4) Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).

The *densities* were determined with a pycnometer of the closed type described by Felsing and Thomas.⁴

The *indices of refraction* were measured with a Zeiss-Pulfrich refractometer, using the D line of sodium. Measurements were made to within 0.02° throughout the temperature range 15 to 35° at one degree intervals to obtain an exact value for dn/dt .

Preparation of Material.—Two c. p. samples of methyl ethyl ketone from different sources were dried for twenty-four hours over anhydrous potassium carbonate (phosphorus pentoxide, concd. sulfuric acid, and even fused calcium chloride were found to cause condensation and decomposition) and then distilled through a chain-packed column (1.8 × 68 cm.), maintaining a 10:1 reflux ratio. The fraction distilling between 79.45 to 79.65° (at 760 mm.), which comprised about three-fourths of the entire distillate, was selected for use. It was stored over anhydrous potassium carbonate; when a portion was desired for use, it was distilled off the carbonate through the fractioning column. All exits were protected against the entry of moisture.

Technical methyl ethyl ketone was dried over anhydrous potassium carbonate and then fractionally distilled repeatedly, using a 10:1 reflux ratio. The fraction distilling between 78.5 and 80.5° was twice purified by the method of Lochte.¹ The solid addition compound was distilled, the distillate dried as before, and the dried product fractionally distilled. The fraction distilling between 79.2 and 79.8° was again subjected to the method outlined and a final product, distilling between 79.45 and 79.65°, was obtained.

The physical constants of these three samples checked remarkably well with each other; the individual determinations of the vapor pressures, densities and indices of refraction of the separate samples fell on the respective composite plots to within the limits of error of the measurements.

Results Obtained.—The *vapor pressures* measured in this investigation cover the temperature range -30 to +80° and may be represented by the relation

$$\log_{10} p(\text{mm.}) = -2644.996/T - 313.0342 \times 10^{-2} \log_{10} T - 403.78573 \times 10^{-5} T + 19.778594$$

which reproduces the observed values to within 1 part in 1000. The calculated normal boiling point is 79.56°; the "I. C. T." value is 79.6°.

The observed *densities* for the range -30 to +85° are represented by the relation

$$d(\text{g./cc.}) = 1.10717 - 103.125 \times 10^{-5} T$$

which reproduces the observed values to within 1 part in 5000, and which is in excellent agreement with some of the later values found in the literature.

The observed *indices of refraction* for the range +15 to +35° are represented by the relation

$$n_D = 1.37799 - 0.000483 (t - 20)$$

This relation reproduces the experimental values to within ±9 in the last decimal place, but it is

only in fair agreement with the few data in existence. Some of the investigators fail to state either their method of purification or of drying; very small amounts of impurities could easily account for the divergence.

Some Derived Quantities.—The exact Clapeyron equation

$$dp/dT = \Delta H_v/T(v_2 - v_1)$$

yields the value of 105.32 cal./g. for the latent heat of evaporation, ΔH_v , while the Thompson⁵ relation yields the value 106.43 cal./g. at the same temperature, the normal boiling point 79.56°. Mathews⁶ cites a direct experimental value of 105.95 cal./g. at 78.20°; the calculated value from the data of this investigation is 105.69 cal./g. at the same temperature.

The molal entropy of vaporization at a vapor concentration of 0.00507 mole per liter, according to Hildebrand,⁷ is calculated to be 27.83 E. U. at 25.90°, where the vapor pressure is 94.66 mm.

Composition of the Addition Compound.—The crystals obtained by treating methyl ethyl ketone with sodium iodide dihydrate by the method of Lochte¹ were dried quickly with filter paper, weighed into a tared flask connected by means of a ground joint to a receiving reservoir, and their volatile matter distilled *in vacuo*, using a carbon dioxide snow-ether mush for cooling and condensation. The weight of the anhydrous sodium iodide residue was then determined and the condensed volatile matter was analyzed by determining its refractive index. The composition was read off a large plot relating indices of refraction to molal composition. In case two liquid layers were obtained as condensate, a definite weight of water was added to the weighed condensate to insure complete miscibility. The volatile content of the crystals ranged from 21 to 40% and the methyl ethyl ketone content of this volatile matter varied from 3.5 to 58%. All possible variations in the concentrations of the components of the system at different temperatures were made and samples from many batches of products were examined in the Geology Department of the University of Texas. However, only *one* form of crystal was found, even when their water-methyl ethyl ketone content ratio was radically different. The contention that Lochte's method of purification was impossible

(5) Thompson, *Chem. News*, **123**, 204 (1913).

(6) Mathews, *THIS JOURNAL*, **48**, 562 (1926).

(7) Hildebrand, "Solubility," Chemical Catalog Co., N. Y., 1924, p. 94.

has been shown to be false; the yield of methyl ethyl ketone, however, is poor and the bisulfite method is to be preferred.

Summary

1. The vapor pressures, densities and refractive indices for pure methyl ethyl ketone, purified

by two methods, have been determined as functions of the temperature.

2. The heat of vaporization and the molal entropy of vaporization have been calculated.

3. The solid addition compound of the ketone and sodium iodide dihydrate has been investigated.

AUSTIN, TEXAS

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The Activated Adsorption of Hydrocarbons

BY JOHN TURKEVICH AND HUGH S. TAYLOR

We have studied the adsorption of ethylene as a typical unsaturated hydrocarbon and methane, ethane and propane as saturated hydrocarbons on typical hydrogenating catalysts. As oxide catalyst we have used the manganese chromite catalyst examined by Taylor and Williamson,¹ for hydrogen and carbon monoxide adsorption. Reduced copper was chosen as a typical metallic catalyst.

Experimental

Apparatus.—The apparatus was of the type used at Princeton for the study of gas adsorption on catalysts.¹ It consisted of a gas-purifying train, a gas buret compensated for variation in atmospheric temperature and pressure, a catalyst tube, a mercury manometer and a pumping system, a mercury diffusion pump backed by an oil pump. Gases desorbed from the catalysts by the mercury vapor pump could also be collected by an automatic Sprengel pump² and fed into a Bone and Wheeler gas analysis apparatus.³ The entire system was made of Pyrex glass except for the soft glass burets, which were attached by ground-glass joints cemented with picene. The gas buret could be read with an accuracy of 0.1 cc. and the pressure reading to 1 mm.. The gas analyses were accurate to 1%.

Preparation of Materials

Manganese Oxide-Chromium Oxide Catalyst.—172 g. of c. p. ammonium chromate was dissolved to make two liters of solution; 234 g. of c. p. manganous nitrate (a 50% solution) was dissolved to make two liters of solution. These two solutions were mixed, allowed to stand for eighteen hours and the supernatant brownish liquor decanted. The precipitate was washed with two liters of 0.2% ammonium nitrate solution and filtered. The residue was suspended in four liters of 0.2% ammonium nitrate solution, decanted and repeatedly washed with 10% ammonium nitrate solution. The suspension was filtered again and dried overnight at 110°. The dry mass was heated gradually to 400° in a muffle furnace and kept there for two hours. The catalyst was reduced *in situ* by hydrogen at

450°. The reduction was considered complete when a tared phosphorus pentoxide tube attached to the exit tube of the catalyst showed no increase in weight after two hours.⁴

Copper Catalyst.—One hundred grams of Kahlbaum copper oxide for organic combustions was slowly reduced *in situ* below 200° by means of hydrogen gas. A long induction period was followed by a fast reduction at about 160°. The temperature was lowered to 120° while the reduction proceeded. The final reduction was made at 200°. Passage of hydrogen was continued until there was no increase during two hours in the weight of a tared phosphorus pentoxide tube attached to the exit tube of the catalyst chamber. The copper catalyst was pumped off for fifty hours at 400° with a mercury diffusion pump and an oil pump.

Gases.—Helium was obtained by passing tank helium through a trap containing activated carbon and immersed in liquid air. The carbon had been evacuated overnight at 500°. Hydrogen prepared electrolytically was passed through a furnace containing platinized asbestos and then dried over calcium chloride and phosphorus pentoxide. Nitrogen from cylinders was passed over metallic copper shavings heated to 500° and dried over phosphorus pentoxide. Ethylene was obtained from cylinders, condensed in a liquid air trap and the middle fraction used. Ethane, analyzing C_{1.87}H_{5.74}, from cylinders, was in part used. For adsorption isotherms, ethane was prepared from hydrogen and ethylene by catalytic reaction over copper. Methane was synthesized from carbon monoxide and hydrogen over nickel, the residual reactants being removed by burning over copper oxide at 350°. The propane was obtained by fractionation of a cylinder product and analyzed C_{3.2}H_{8.4}.

Temperature Control.—Vapor baths were used above 0°. Liquid air, solid carbon dioxide and ether, and ice were used for the low temperature work, an oxygen thermometer recording the exact temperature with liquid air.

Procedure

The dead space in the catalyst tube was determined by the measurement of the volume of helium added and the pressure of the gas produced in the catalyst tube. The method of calculation was that explained by Williamson.⁴ The validity of the assumption that no helium was adsorbed, was tested by measuring the helium isotherms at

(1) Taylor and Williamson, *THIS JOURNAL*, **53**, 2168 (1931).

(2) Dunoyer "Vacuum Practice," G. Bell and Sons, London, 1926.

(3) Bone and Wheeler, *J. Soc. Chem. Ind.*, **28**, 10 (1908).

(4) Williamson, Thesis, Princeton University, 1931.