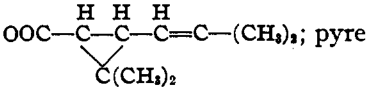
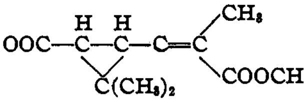
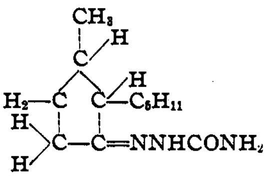
them to differ sharply with respect to their solubility in acids. The semicarbazones which we have considered may be divided into two groups, those that are soluble and those that are insoluble in dilute hydrochloric acid.

The former include the semicarbazones of pyrethrone, formula I, R = C_5H_7, R′ = H; dihydropyrethrone (jasmone), R = C_5H_9, R′ = H; tetrahydropyrethrone (dihydrojasmone), R = C_5H_{11}, R′ = H; and tetrahydropyrethrolone, R = C_5H_{11}, R′ = OH. The acid-insoluble semicarbazones include those of pyrethrolone, formula I, R = C_5H_7, R′ = OH; pyrethrin I, R = C_5H_7, R′ =  $\mathrm{OOC{-}\underset{\diagdown\diagup\ C(CH_3)_2}{\overset{H}{C}{-}\overset{H}{C}}{-}\overset{H}{C}{=}C{-}(CH_3)_2}$; pyrethrin II, R = C_5H_7, R′ =  $\mathrm{OOC{-}\underset{\diagdown\diagup\ C(CH_3)_2}{\overset{H}{C}{-}\overset{H}{C}}{-}C{=}C{\Large\langle}^{CH_3}_{COOCH_3}}$ and two geometric forms of hexahydropyrethrone semicarbazone of melting points 160 and 194°, respectively, represented by formula II.



II

There seems to be no chemical feature distinguishing the members of each group. The solubility of some of the semicarbazones has been utilized in their separation from other material. All of an acid-soluble semicarbazone present in an impure reaction mixture may be obtained practically pure by extraction with dilute hydrochloric acid, removal of the by-products with a water-immiscible solvent, and precipitation of the semicarbazone with alkali. For example, a reaction product consisting of tetrahydro- and hexahydropyrethrone semicarbazones was separated into the two components by dissolving the one in dilute acid and filtering from the other.

To what extent the property of solubility in hydrochloric acid is shared by the semicarbazones of other ketones is a matter of interest, but one which we have not investigated.

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Photoreaction of Chlorine Monoxide and Hydrogen

BY T. IREDALE AND T. G. EDWARDS

According to Finkelnburg, Schumacher and Stieger[1] chlorine monoxide dissociates, in the continuous absorption region of the visible spectrum, into Cl and ClO. We have found that addition of hydrogen accelerates the decomposition, at any rate, up to the stage where the secondary reaction $H_2 + Cl_2 = 2HCl$ becomes prominent. As without the H_2, Cl_2 and O_2 are the main products, but there are now also small amounts of HCl and H_2O. Finally all the Cl_2 goes to HCl.

Since the reaction $Cl + H_2 = HCl + H$ has a collision efficiency of 10^{-4} — 10^{-5}, and $Cl + Cl_2O = Cl_2 + ClO$[1] a collision efficiency of $10^{-2} - 10^{-3}$, H atoms are not so important as the ClO radical in continuing the chain, that is, where the Cl_2O and H_2 pressures are comparable. The chain must, therefore, be continued by the reactivity of ClO and H_2, a state of affairs not much understood in the literature of this subject.

We may have either $ClO + H_2 = HClO + H$ or $ClO + H_2 = HCl + OH$. The latter reaction seems the more probable. Further details will be forthcoming when we have studied the reaction more closely.

Contrary to the experience of others,[2] we did not find that Cl_2O was explosively unstable in the presence of strong light. A 500 candle power lamp brought within 2.5 cm. of a spherical glass bulb (7.6 cm. in diameter) containing Cl_2O at a pressure of half an atmosphere, did not cause an explosion, nor did it do so when hydrogen was present at the same pressure.

(1) Finkelnburg, Schumacher and Stieger, *Z. physik. Chem.*, **B15**, 127 (1931).

(2) Wallace and Goodeve, *Trans. Faraday Soc.*, **27**, 653 (1931).

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The Heat of Mixing of Diisobutylene and Isooctane

BY WM. D. KENNEDY AND GEORGE S. PARKS

In connection with the recent study by Crawford and Parks[1] of the liquid-phase hydrogenation of diisobutylene (*i. e.*, a material containing about 4 parts of 2,4,4-trimethylpentene-1 and 1 part

(1) B. L. Crawford and G. S. Parks, THIS JOURNAL, **58**, 373 (1936).

of 2,4,4-trimethylpentene-2) to yield isoöctane (2,4,4-trimethylpentane), the assumption was made that mixtures of this paraffin with the parent olefins formed practically "perfect" solutions. Accordingly such solutions should be formed from the components without any appreciable heat of mixing and the partial vapor pressures of the components should follow Raoult's law. In view of the structural similarity of the paraffins and the olefins here involved, this assumption of perfect solutions certainly appeared reasonable on *a priori* grounds. Moreover, Beatty and Calingaert[2] had shown that the total pressures of mixtures of *n*-heptane and *n*-heptene-3 near the boiling point do not exhibit at any concentration more than a 0.5% positive deviation from the requirements of Raoult's law. However, the departure from ideality of such solutions may be appreciably greater at lower temperatures. In view of this possibility and the simplicity of the measurements, we decided to make also some direct calorimetric determinations of the heats of mixing of diisobutylene and isoöctane.

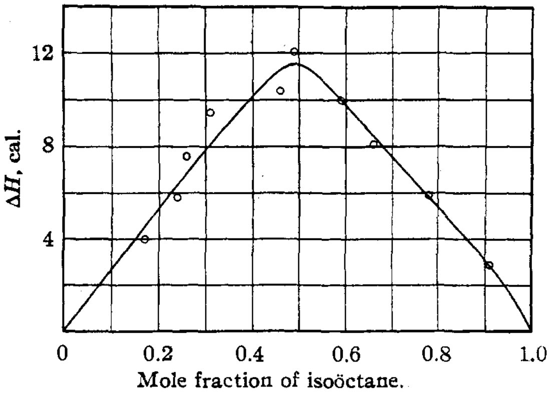

Fig. 1.—The heat absorption per mole of solution formed plotted against the mole fraction of isoöctane.

The vacuum jar calorimeter and the method of mixing employed previously by Parks and Chaffee[3] were used again in the present study. The mixing took place at 23° and the temperature change on formation of the solutions was measured to 0.001° by a copper–constantan thermocouple in conjunction with a White potentiometer. The necessary specific heat data for isoöctane and diisobutylene were taken from previous studies[4] in this Laboratory. Our hydrocarbon samples were carefully prepared materials which had been presented to us by the Shell Development Company. They had boiling ranges of about a degree and crystallized completely when cooled with liquid air; the respective densities at 20° were 0.6912 for the isoöctane and 0.7168 for diisobutylene.

Ten separate determinations of the heat of mixing were made in forming solutions ranging from 0.17 to 0.91 mole fraction of isoöctane. In the isothermal mixing process there appeared, for all concentrations, a small endothermic effect, which we have represented graphically in the accompanying figure. In our experiments this heat absorption reached a maximum for the formation of a solution containing 0.49 mole fraction of the isoöctane. In this case we found $\Delta H_{296} = 12.1\ (\pm 1.0)$ cal. for the process

$$0.49\ C_8H_{18}(l) + 0.51\ C_8H_{16}(l) = 1 \text{ mole of solution}$$

The minuteness of such a heat effect can be further emphasized by noting that it is only 1.3% of the effect previously recorded in the formation of a comparable solution of benzene and *n*-hexane.[5]

The previous assumption that such diisobutylene–isoöctane solutions are practically perfect is thus well justified.

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[2] H. A. Beatty and G. Calingaert, *Ind. Eng. Chem.*, **26**, 505 (1934).

[3] G. S. Parks and C. S. Chaffee, *J. Phys. Chem.*, **31**, 439 (1927).

[4] G. S. Parks, H. M. Huffman and S. B. Thomas, THIS JOURNAL, **52**, 1032 (1930); G. S. Parks and H. M. Huffman, *ibid.*, **52**, 4381 (1930).

[5] "International Critical Tables," Vol. V, page 157.

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The Transport Number of Silver in Solutions of Sodium Thiosulfate Practically Saturated with Silver Chloride

BY PIERRE VAN RYSSELBERGHE AND S. M. KNAPP

Evidence obtained by Müller and by Carrière and Raulet[1,2] from electrometric titration and conductivity shows that in aqueous mixtures of sodium thiosulfate with a silver salt, the silver is present as a monovalent anion $AgS_2O_3^-$.

We have obtained direct evidence for the existence of such an ion by measuring the transport number of silver in solutions of sodium thiosulfate saturated with silver chloride at 23°. The experiments were run at 25° according to a technique similar to that of Van Rysselberghe

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[1] Müller, *Z. anorg. Chem.*, **133**, 202 (1924).

[2] Carrière and Raulet, *Compt. rend.*, [7] **192**, 423 (1931).