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Study on Synthetic Methods of Trialkyl Phosphate Oxide and Its Extraction Behavior of Some Acids

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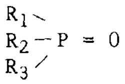
ABSTRACT

Trioctyl phosphine oxide (TOPO) is useful for the extraction of many inorganic and organic compounds. A mixed trialkyl phosphine oxide (TRPO)



$$\begin{matrix} R_1 \searrow & \\ R_2 - & P = 0 \\ R_3 \nearrow & \end{matrix}$$

(where R_1, R_2, and R_3 are different alkyl groups) is similar in property to TOPO. The total number of carbon atoms per molecule of TRPO ranges from 15 to 27. Three methods for synthesizing TRPO are described in this paper. When TRPO is synthesized from an alcohol mixture it is significantly cheaper than a single pure alcohol as required for the production of TOPO; tedious purification steps are eliminated. TRPO is a brown liquid which is very slightly soluble in water. Toxicological measurements of LD50, AMES test, hereditary and accumulative toxicity show that TRPO is safe for use in the extraction of some pharmaceutical and biochemical compounds.

Examinations of IR and NMR show that the complex interaction of P=0 bond of TRPO with extracted substances is the same as that of TOPO. The distribution coefficients of phosphoric acid, citric acid, malic acid, oxalic acid, and tartaric acid with TRPO are reported. The extraction of these acids is believed to proceed by neutral-complex mechanism.

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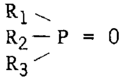
INTRODUCTION

Neutral phosphoryl compounds have been applied extensively in extraction processes. Neutral phosphates can be divided into four classes — $(RO)_3PO$, $RPO(OR)_2$, $R_2P(O)OR$, and R_3PO according to the degree to which the hydroxyl function in phosphoric acid is replaced with alkyl groups. By using a Hückel molecular orbital (HMO) method, C. Y. Yuan (1) proved that in these four classes of neutral phosphates, the charge density of phosphoryl oxygen (q_o) and phosphorus atoms (q_p) is the highest in R_3PO, but the overall π energy ($\Sigma\gamma_i$) and π bond energy of phosphoryl oxygen is a main factor influencing extraction ability. The trialkyl phosphoryl oxygen is a main factor influencing the extraction ability of trialkyl phosphine oxide [e.g., trioctyl phosphine oxide (TOPO)], a useful extractant in many industries. But the high cost of TOPO (2) has limited its use. TRPO is the class of mixed trialkyl phosphine oxides with the general formula



$$R_1R_2R_3P = O$$

where R_1, R_2, R_3 are the same or different alkyl groups with 5 to 9 carbon atoms respectively, and the total number of carbon atoms per molecule then ranges from 15 to 27. The starting material for preparing TRPO can be the inexpensive by-product of high-grade lubricant production, while the polymerization catalyst and starting materials for preparation of TOPO are very expensive (3). Since the raw material cost of TRPO is much lower than that for a single trialkyl phosphine oxide such as TOPO; TRPO has been produced and used in the nuclear industry in China since the 1960s.

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Use of mixed substances as extractants has also been applied elsewhere on an industrial scale (4). After the average molecular weight, the ratio of carbon to hydrogen, and the IR spectrum of mixtures have been determined, the quality of the mixed extractant can be assessed. Extraction techniques using TRPO have been used recently for the recovery of citric acid, purification of wet-process phosphoric acid etc. TRPO has become regarded as a good extractant with numerous potential applications, and it has been receiving increasing attention recently.

SYNTHESIS METHODS

The synthesis methods of TRPO can follow any of three paths:

(1) Oxidation of Trialkyl Phosphine

The reaction can be written as follows:

$R_3P + (o) = R_3PO$.

In this method the R_3P is produced by reaction of alkenes and phosphine (PH_3). PH_3 is a toxic gas and will burn in air; so this method is not used in China on an industrial scale.

(2) Synthesis from Phosphorus and Bromine

A mixture of monohydroxyl alcohols having the boiling range of 160-180°C is first reacted with bromine. The alkyl bromide is then reacted with phosphorus at 205-210°C in the presence of bromine to form a complex compound which can be hydrolyzed by nitric acid at 70°C to produce a crude TRPO. The crude product can be purified by vacuum distillation. This method was invented by Kealsonov in the U.S.S.R. in 1960 (4).

(3) Grinard Reagent Method (5)

The same mixture of monohydroxyl alcohols used in method 2 can be reacted with chlorine sulfoxide in the presence of DMF to form alkyl chlorides. Then when magnesium powder is added to the reactor in the presence of ether, the Grinard reagent formed is reacted with phosphorus oxytrichloride ($POCl_3$) to form a crude TRPO suitable for purification by vacuum distillation.

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The key to this method is effective expelling of the water and alcohol while the Grinard reagent is being reacted; otherwise an intense explosion can occur. The authors have solved the problem by using adsorption techniques. The Grinard reagent method has been applied on an industrial scale in China.

Preparation methods for TOPO can be found in the literature (6), and they consume purified chemicals, such as octyl ether, magnesium, iodine, sodium carbonate, $POCl_2$ etc., and produce by-products phosphoric acid. Also more operation steps are required in the preparation of TOPO than in preparation of TRPO.

MEASUREMENT OF PHYSICAL PROPERTIES AND EXTRACTION ABILITY OF TRPO

The measured physical properties of TRPO are listed in Table 1. Table 1 shows that the physical properties of TOPO are different from those of TRPO. For example, TRPO is a white liquid whose boiling point is 187°C, but TOPO is a white crystal with a melting point of 48°C and a boiling point of 180-205°C (7).

If TRPO is to be used for extraction of edible substances, the first consideration is its toxicity. The LD50 value of TRPO is 3370 mg/kg; this can be regarded as low toxicity. TRPO can pass "AMES" and hereditary as well as accumulative tests; so TRPO is suitable for extraction in the pharmaceutical and food industries.

Using odorless kerosene as the diluent, extractions of phosphoric acid, citric acid ($C_6H_8O_7$), oxalic acid ($H_2C_2O_4$), tartaric acid ($H_2C_4O_2$), malic acid ($C_4H_4O_4$), and lactic acid ($C_3H_6O_3$) were studied

TABLE 1
Physical Properties of TRPO

Average molecular weight	312	Color	White
Refractive index (n_0^{20})	1.4600	Odor	Little scorched
Density (n_0^{20})	0.880	Carbon, %	71.26
Solubility in water (g/l)	0.090	H, %	12.55
IR (cm^{-1})	1150 (γ_p=0)		

TABLE 2
Distribution Coefficients
T = 303 K

TRPO % (V/V)	H_3PO_4	$C_6H_8O_7$	$H_2C_2O_4$ (8)	$H_2C_4O_2$ (9)	$H_4C_4O_4$	$H_6C_3O_3$
100	0.61	7.61	53.2	2.77	2.35	2.10
80	0.50	3.87	42.6	1.45	1.46	1.73
65	0.35	2.03	19.0	1.13	1.07	1.30
50	0.31	1.23	13.9	0.73	0.53	0.86
30	0.27	0.77	4.69	0.44	0.46	0.49

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in separating funnels and AKUFVE system under different conditions. When the phase ratio, O/A, is unity and the contact times are long enough that extraction equilibrium is attained, the distribution coefficients are shown in Table 2.

All of the acids tested, except phosphoric acid, are organic acids. The molecular structures of these organic acids are similar. Table 3 shows the relationship between atomic ratios of carbon to oxygen (C/O) and distribution coefficients. As the ratio C/O decreases, the distribution coefficient D increases. This is worthy of further study.

Comparisons of acid extraction using the same concentration of TRPO and TOPO are shown in Table 4, and the extraction ability of TRPO is shown to be about the same as that of TOPO.

DISCUSSION OF EXTRACTION COMPLEX PROCESS

Extraction of acids by TRPO is considered to involve formation of a neutral complex

$$H_nA + pTRPO + rH_2O = H_nA \cdot pTRPO \cdot rH_2 \ . \qquad (1)$$

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TABLE 3
The Relationship Between C/O and D
T = 303 K

Acid	Molecular formula	C/O Value	D
Tartaric	$H_2C_4O_2$	2.0	2.77
Malic	$H_4C_4O_4$	1.0	2.35
Lactic	$H_6C_3O_3$	1.0	2.10
Citric	$C_6H_8O_7$	0.857	7.61
Oxalic	$H_2C_2O_4$	0.50	53.2

TABLE 4
The Comparison of Extraction Ability Between TOPO AND TRPO

Solvent	Concentration in org. phase (M)	Acid	Concentration in liq. phase (M)	D
TOPO (2)	0.21	Citric	0.21	0.01
TRPO	0.23	Citric	0.21	0.03
TOPO	0.35	Phosphoric	0.36	0.35
TRPO	0.35	Phosphoric	0.38	0.37
TOPO (10)	0.20	Acetic	0.30	1.46
TRPO	0.23	Acetic	0.30	1.22

The equilibrium (concentration) constant of extraction can be expressed by the following equation

$$K_{ex} = \frac{[H_nA \cdot pTRPO \cdot rH_2O]}{[H_nA][TRPO]^p} \; . \qquad (2)$$

The distribution ratio D is defined as $\frac{[H_nA \cdot pTRPO \cdot rH_2O]}{[H_nA]}$; so

$$D = K_{ex}(TRPO)^p \; . \qquad (3)$$

Substituting the values of Table 2 into Eq. (3), the complex ratio p can be determined.

In Fig. 1 the IR spectra of TRPO and the complex formed from TRPO and citric acid are shown. It is found that $\gamma_{P=0}$ for TRPO moves towards lower frequencies as the complexes are formed, i.e., from $\gamma_{P=0}$ = 1150 cm^{-1} to 1125 cm^{-1}, and $\Delta\gamma_{P=0}$ = 25 cm^{-1}.

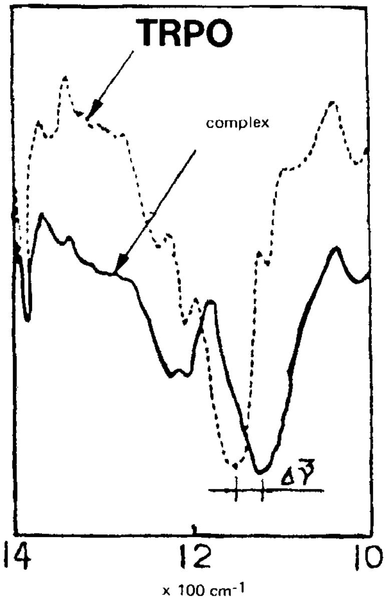

Fig. 1. IR spectra.

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The proton NMR spectra were also studied, and the results are shown in Fig. 2. The difference or chemical shift of the peak for TRPO is $\Delta\delta = 0.35$ ppm (from $\delta = 3.20$ ppm for pure TRPO to 2.85 ppm for the complex of TRPO and citric acid).

The differences in the sign and magnitude of IR peak and NMR chemical shift indicate that the P=O bond of TRPO exerts strong coordination force and possesses high extracting power.

ENTHALPY DATA

The enthalpy change of the extraction process may be determined as follows:

$$K = K_0 \exp(-\Delta H/RT) \ . \qquad (4)$$

Then

$$\ln K = \ln K_0 + (-\Delta H/R)(1/T) \ . \qquad (5)$$

Because the distribution coefficient D is proportional to the equilibrium constant K,

$$\ln D = \ln D_0 + (-\Delta H/R)(1/T) \ . \qquad (6)$$

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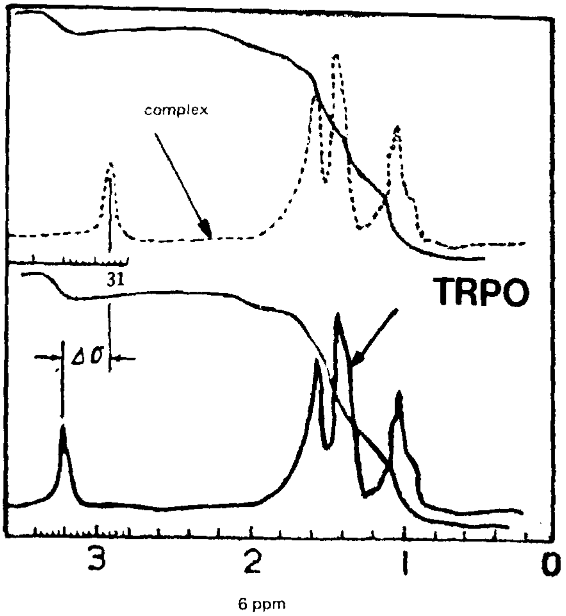

Fig. 2. Proton NMR.

TABLE 4
Distribution Coefficient under Different Temperature

Temperature °C	12	25	30	50	65	80
Citric acid	9.72	7.61	7.33	5.91	4.40	2.91
Oxalic acid	71.5	60.6	53.2	39.1	27.6	18.7

In the temperature range between 15° and 80°C, D values for citric acid and oxalic acid are shown as Table 4.

From these, the following values may be determined for citric acid:

$$\log D = 0.073 \times 10^{4}(1/T) + 8.78$$

$$\Delta H = -14.02 \text{ KJ/mol} .$$

(The correlation coefficient is 0.813; the degree of reliance is 0.05; and the critical correlation coefficient is 0.811).

TABLE 5

ΔH Values Measured

%, TRPO (V/V in the organic phase)	30	50	65	80
Number of measurements	6	5	5	5
Correlation coefficient	0.988	0.951	0.945	0.867
ΔH, KJ/mol	-15.90	-9.25	-10.42	-5.86

For oxalic acid:

$$\log D = 0.233 \times 10^4 (1/T) - 6.31$$

$$\Delta H = -19.38 \text{ KJ/mol}$$

(The correlation coefficient is 0.995; the degree of reliance is 0.05; and the critical correlation coefficient is 0.811).

Both extraction processes are exothermic, and the enthalpy change ($-\Delta H$) is in agreement with that expected for forming complexes through a hydroxyl group.

For extraction of citric acid, the ΔH values were determined for different percentages of extractant in the organic phase, and the results are listed in Table 5.

All extraction processes with different TRPO concentrations in the organic phases are exothermic, but no functional relationship has been found between the ΔH values and the composition of the organic phase. In extraction processes the concentrations of aqueous and organic phase change continuously. Evaluation of the activity coefficient is complicated, e.g., the activity coefficient of the extractant in the organic phase is usually unknown (11). Thus discussion of thermodynamics of extraction equilibrium are often regarded as little more than guesswork.

CONCLUSIONS

(1) Three synthetic methods of TRPO, namely oxidation of trialkyl phosphine, synthesis from phosphorus and bromine, and Grinard reagent methods, have been discussed, and the Grinard reagent method has been found to be suitable for industrial production in China.

(2) By measuring several physical and chemical properties, especially toxic tests, it is evident that TRPO can be used as an extractant in food and pharmaceutical industries.

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(3) Distribution coefficients of phosphoric acid and organic acids were measured and are reported. IR and NMR studies indicate that the complex reaction is mainly due to the P=O bond in TRPO.

(4) Enthalpy changes during extractions of citric acid and oxalic acid have been studied, and the values are reported.

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