

$R_2 = H$), 112-44-7; $R^1R^2C=O$ ($R^1 = PhCH=CH$; $R_2 = H$), 14371-10-9; $R^1R^2C=O$ ($R^1, R^2 = c-C_5H_{10}$), 108-94-1; $R^1R^2C=O$ ($R^1 = CH_3$; $R^2 = Me_2C=CH(CH_2)_2$), 110-93-0; $R^1R^2C=O$ ($R^1 = c-C_6H_{11}$; $R^2 = H$), 2043-61-0; $R^1R^2C=O$ ($R^1 = i-Pr$; $R^2 = H$), 78-84-2; $R^1R^2C=O$ ($R^1 = t-Bu$; $R^2 = H$), 630-19-3; trichlorovinylsilane, 75-94-5; α -bromovinyltrichlorosilane, 18038-34-1; acetic anhydride, 108-24-7; trifluoroacetic anhydride, 407-25-0; $SOCl_2$, 7719-09-7.

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Oxidation of Hydrocarbons. 8. Use of Dimethyl Polyethylene Glycol as a Phase Transfer Agent for the Oxidation of Alkenes by Potassium Permanganate^{1a}

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Dimethyl polyethylene glycol solubilizes potassium permanganate in benzene or methylene chloride and can thus be used as a phase transfer agent for permanganate oxidations. If benzene is used as the solvent, dimethyl polyethylene glycol will not efficiently extract potassium permanganate from an aqueous solution, but it will solubilize the solid reagent. When methylene chloride is used as the solvent, potassium permanganate may be transferred from either an aqueous solution or from the solid phase. The products obtained from the oxidation of terminal alkenes were found to be the corresponding carboxylic acids with one less carbon, while nonterminal alkenes gave diones, diols, and ketols as well as carboxylic acids. The distribution of products may be controlled through selection of the appropriate conditions. A comparison has been made with the use of a quaternary ammonium ion, a crown ether, and acyclic polyethers as phase transfer agents for the oxidation of alkenes by permanganate.

Historically the use of permanganate ion as an oxidant for hydrocarbons has been limited because of its low solubility in most nonpolar solvents.^{1b} However, the observation that potassium permanganate could be extracted from water into benzene by use of phase transfer agents substantially increased the potential usefulness of this reagent. The first phase transfer agent used was tricaprilmethylammonium chloride.² Since that time other ammonium³⁻⁵ and arsonium⁶ salts have been used with varying degrees of success. In 1967 Pedersen⁷ reported that crown ethers could also be used to solubilize potassium permanganate in benzene, and Sam and Simmons⁸ later observed that excellent yields could be obtained from the oxidation of organic compounds in these solutions. This method, although highly efficient, has not been widely applied, probably because of the rather high cost of crown ethers.

The work described in this report was originally designed to compare, under identical conditions, the usefulness of crown ethers and quaternary ammonium salts as phase

transfer agents for permanganate oxidations. However, during the course of the study we were informed of work from Lehmkuhl's laboratory which indicated that dimethyl polyethylene glycols could also be used as phase transfer agents for potassium permanganate.⁹ Consequently the scope of the study was enlarged to evaluate the usefulness of dimethyl polyethylene glycol in relationship to a typical quaternary ammonium ion phase transfer agent (Adogen 464) and a typical crown ether (dicyclohexano-18-crown-6) for the oxidation of alkenes.

The linear phase transfer agents (which Lehmkuhl called "Schleifenathers",¹⁰ but which are also known as "glymes"¹¹) consisted of a mixture of dimethyl polyethylene glycols with dimethyl octaethylene glycol as the principal component.¹² Previous work had shown that polyethers formed complexes with various cations,¹³ and Lehmkuhl et al. have used them effectively as phase transfer agents for nucleophilic substitution reactions.¹⁴

In more recent studies (where these and other complexing

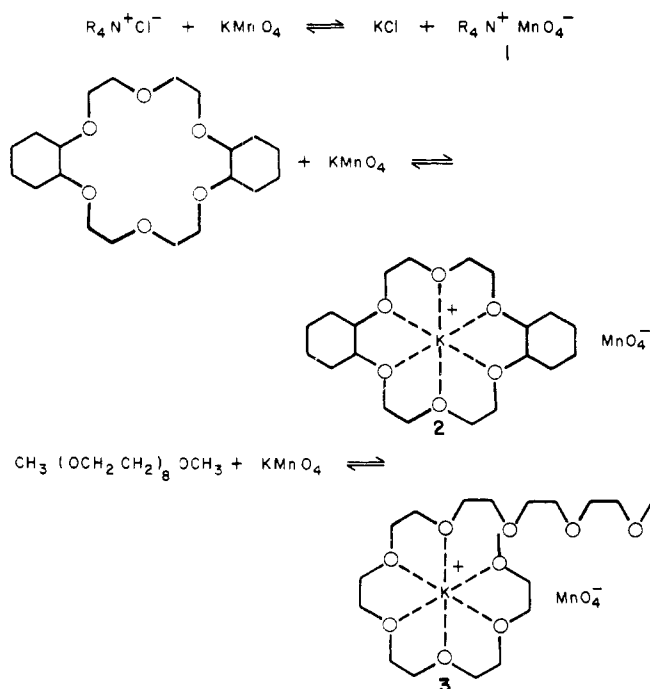


Figure 1.

agents have been referred to as "hosts"), Cram and his co-workers have compared the complexing abilities of crown ethers and the corresponding noncyclic compounds.¹⁵ In general, they found that preorganization into a crown increases the amount of complex present, but nonconverging systems are also induced to form ordered arrangements of binding sites in the presence of cations. This leads to the formation of complexes, albeit with somewhat lower binding energies.

Results and Discussions

The phase transfer equilibria involved in the reactions under consideration may be visualized as in Figure 1. Of the products depicted only 2 has been isolated and characterized.⁸ It is possible that 3 has a greater complexity than indicated. For example, models show that it is possible for the oxygens to arrange themselves about the central ion in a nonplanar fashion. Furthermore, Bush and Truter¹⁶ have shown that a crown ether containing ten oxygens wraps itself around the potassium ion in a pattern similar to the seam of a baseball.

Initial experiments indicated quite clearly, however, that this acyclic polyether could not be used to extract aqueous potassium permanganate into a nonpolar solvent such as benzene. Instead of bringing the permanganate ion into solution in the nonaqueous phase, it appears that the polyether moved into the aqueous phase and slowly reduced the oxidant. To overcome this problem we have used a modification of the procedure described by Sam and Simmons⁷ wherein solid potassium permanganate is brought into solution directly without first dissolving it in water. When dimethyl polyethylene glycol is added to an organic solvent along with pulverized potassium permanganate, a transfer from the solid to the liquid phase takes place, and any alkene present is oxidized. This provides for a very simple procedure that gives products in good yields and high purity.

It is apparent that the oxygens in 3 would be more exposed than those in 2, and this may explain why 3 cannot be used to transfer permanganate from an aqueous phase into benzene. The available oxygens would be hydrophilic, and thus the complex would be more soluble in the aqueous solution.

The fact that the dimethyl polyethylene glycol complex is

Table I. Oxidation of 1-Decene^a

Solvent system	Phase transfer agent	Products (%)
Benzene plus 10% acetic acid	Polyether ^b	Nonanoic acid (80)
Benzene plus 10% acetic acid	Crown ether ^c	Nonanoic acid (80), octanoic acid (5)
Benzene plus 10% acetic acid	Adogen 464	Nonanoic acid (90), octanoic acid (4)
Benzene/water plus 8% acetic acid	Adogen 464	Nonanoic acid (90), octanoic acid (5)
Benzene/water	Polyether ^b	Nonanoic acid (10), 1-decene (90)
Methylene chloride/water plus 8% acetic acid	Polyether ^b	Nonanoic acid (95)

^a The reactions were conducted at room temperature using 4 mol of potassium permanganate per mole of alkene. ^b Dimethyl polyethylene glycol. ^c Dicyclohexano-18-crown-6.

more soluble in water than in benzene can be used to advantage during the purification of products. If the benzene solution is extracted with water, all but traces of the phase transfer agent are removed, making it easier to distill or crystallize the product. In fact, a reasonably pure product is often obtained simply by flash evaporation of the solvent, whereas use of quaternary ammonium salts or crown ethers always gives initial products contaminated by the phase transfer agent.

However, if a more polar organic solvent such as methylene chloride is used along with dimethyl polyethylene glycol, potassium permanganate may be extracted from an aqueous solution. Although use of this medium gives an initial product contaminated by the phase transfer agent, it is a superior solvent in almost every other way. It is more volatile (and thus more easily removed), less expensive, and more resistant to oxidative degradations. Foglia et al.⁵ also found that methylene chloride was a better solvent than benzene when used in conjunction with aqueous permanganate and a phase transfer agent.

The products obtained from the oxidation of three different alkenes have been compared in Tables I-III. It can be seen that the yields obtained by the use of dimethyl polyethylene glycol compare well with those produced using other phase transfer catalysts. In fact, the highest yield of nonanoic acid was obtained from the oxidation of 1-decene in methylene chloride using dimethyl polyethylene glycol in conjunction with aqueous permanganate (Table I). The same procedure also gave the highest yield of 5,6-decanedione from the oxidation of *trans*-5-decene (Table II) and a very good yield of dodecanedioic acid from the oxidative cleavage of cyclododecene (Table III). On the other hand, we were not able to obtain any diol from the oxidation of *trans*-5-decene using dimethyl polyethylene glycol in conjunction with alkaline aqueous permanganate (Table II), whereas the other phase transfer agents gave diols in about 20% yields. Other alkenes have been reported to give diols in yields of 50-80% when this procedure was used with quaternary ammonium salts or crown ethers.^{3,5}

The formation of diones during the oxidation of nonterminal alkenes (Tables II and III) is of interest because they have not previously been reported as products from aqueous permanganate oxidations.^{1b} The only report of the production of diones in substantial quantities was made by Sharpless et al.¹⁷ in 1971. They found that diones were formed when nonterminal alkenes were oxidized by potassium permanganate in acetic anhydride solutions. We have also noted the forma-

Table II. Oxidation of *trans*-5-Decene^a

Solvent system	Phase transfer agent	Products (%)
Benzene plus 15% acetic acid	Polyether ^b	Valeric acid (69), 5,6-decanedione (28)
Benzene plus 15% acetic acid	Adogen 464	Valeric acid (59), 5,6-decanedione (20)
Benzene plus 15% acetic acid	Crown ether ^c	Valeric acid (44), 5,6-decanedione (36)
Methylene chloride/water plus 8% acetic acid	Polyether ^b	Valeric acid (45), 5,6-decanedione (53)
Methylene chloride/aqueous sodium hydroxide	Polyether ^b	Valeric acid (43), 5,6-decanedione (7), 5-hydroxy-6-decanone (11), 5-decene (20)
Methylene chloride/aqueous sodium hydroxide	Crown ether ^c	Valeric acid (3), 5,6-decanedione (2), 5-hydroxy-6-decanone (30), 5,6-decanediol (19), 5-decene (10)
Methylene chloride/aqueous sodium hydroxide	Adogen 464	Valeric acid (26), 5-hydroxy-6-decanone (11), 5,6-decanediol (20), 5-decene (14)

^a The reactions were conducted at room temperature using 3 mol of oxidant per mole of alkene. ^b Dimethyl polyethylene glycol. ^c Dicyclohexano-18-crown-6.

tion of diones where acetone is used as a solvent¹⁸ and have therefore come to the conclusion that their formation is promoted by the use of nonaqueous solvents. In the presence of water a reaction intermediate, such as a ketol, is apparently intercepted and converted into one of the products more commonly found in aqueous permanganate oxidations.

Mechanistic studies of the oxidation of alkenes in aqueous solutions have indicated that ketols are formed by the reaction sequence depicted in Scheme I.^{1b,19} In the absence of water the hydrolysis of **5** would be prevented, and it could quite conceivably undergo further reaction with oxidant to give the dione as suggested in Scheme II. The oxidation of **5** has been depicted as a hydrogen atom abstraction process in analogy with the oxidation of alcohols,^{1b} although a hydride transfer would also result in dione formation.

It has been noted by Krapcho et al.²⁰ that the addition of

Scheme I

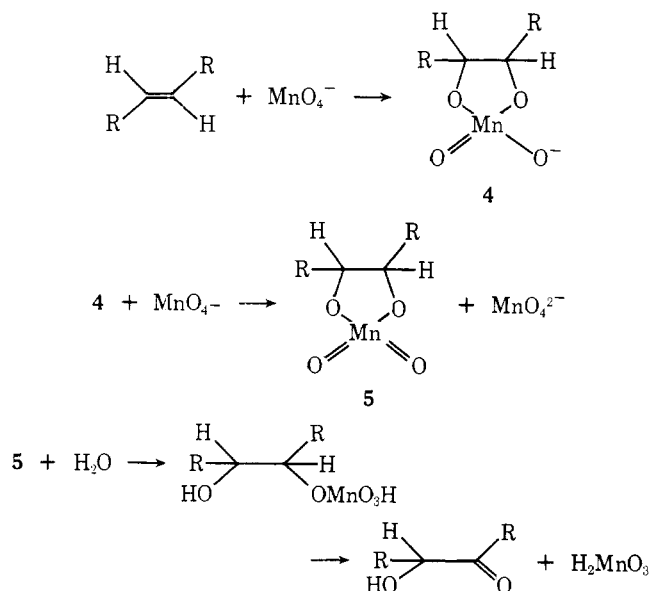
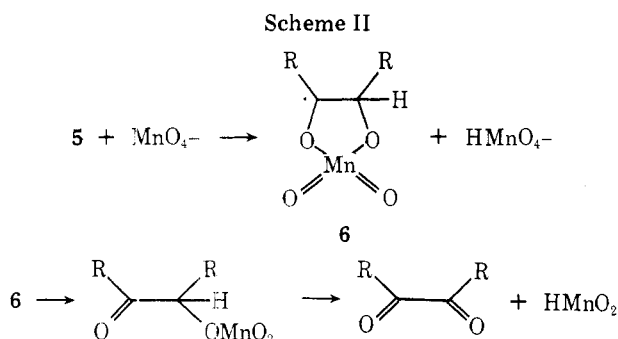


Table III. Oxidation of Cyclododecene

Solvent system	Oxidant ratio ^a	Phase transfer agent	Products (%)
Benzene plus 17% acetic acid	3.3	Polyether ^c	1,2-Cyclododecanedione (16), dodecanedioic acid (59), cyclododecene (23)
Benzene plus 17% acetic acid	3.3	Crown ether ^d	1,2-Cyclododecanedione (22), dodecanedioic acid (56), cyclododecene (12)
Benzene plus 17% acetic acid	3.3	Adogen 464	1,2-Cyclododecanedione (8), dodecanedioic acid (58), cyclododecene (9)
Methylene chloride plus 17% acetic acid	3.3	Polyether	1,2-Cyclododecanedione (8), dodecanedioic acid (77), cyclododecene (1)
Methylene chloride plus 17% acetic acid	3.3	Crown ether	1,2-Cyclododecanedione (7), dodecanedioic acid (83), cyclododecene (3)
Methylene chloride plus 17% acetic acid	3.3	Adogen 464	1,2-Cyclododecanedione (7), dodecanedioic acid (83), cyclododecene (2)
Methylene chloride plus 17% acetic acid	2.2	Adogen 464	1,2-Cyclododecanedione (18), dodecanedioic acid (63), 2-hydroxycyclododecanone (6), cyclododecene (6)
Methylene chloride plus 17% acetic acid	1.6	Adogen 464	1,2-Cyclododecanedione (14), dodecanedioic acid (40), 2-hydroxycyclododecanone (6), cyclododecene (23)
Methylene chloride plus 7% acetic acid	2.2	Adogen 464	1,2-Cyclododecanedione (19), dodecanedioic acid (27), 2-hydroxycyclododecane (7), cyclododecene (23)
Methylene chloride/water plus 10% acetic acid	2.2	Adogen 464	1,2-Cyclododecanedione (69), dodecanedioic acid (13), 2-hydroxycyclododecane (3), cyclododecene (9)
Methylene chloride/water plus 10% acetic acid	2.2	Polyether ^c	1,2-Cyclododecanedione (16), dodecanedioic acid (82)
Methylene chloride/aqueous NaOH	1.0	Benzyltriethylammonium chloride	1,2-Cyclododecanediol (50) ^b

^a Number of moles of potassium permanganate per mole of alkene. ^b Reference 3. ^c Dimethyl polyethylene glycol. ^d Dicyclohexano-18-crown-6.



acetic acid prevents formation of overoxidation products when terminal alkenes are cleaved by permanganate ion. For example, they have reported that the oxidation of 1-octene by permanganate ion in a two-phase water/pentane system containing a phase transfer catalyst gives about 10% hexanoic acid in addition to the major product, heptanoic acid. Addition of a few milliliters of acetic acid decreased the amount of hexanoic acid formed and increased the yield of heptanoic acid.

The reduction of permanganate produces hydroxide ions which, in the absence of acetic acid, probably promote the overoxidation reaction in some way. The production of hydroxide ion when powdered potassium permanganate is used in a nonaqueous system also interferes with the progress of the reaction because the reduction product becomes a sticky gelatinous mass of manganese(IV) hydroxide that is difficult to filter and which may occlude considerable quantities of permanganate ion as it precipitates. This often brings the reaction to a premature termination with a great deal of unreacted starting material remaining. We have found that the addition of sufficient acetic acid to neutralize the hydroxide ions formed alleviates this problem and thus promotes a more complete reaction.

The use of solid potassium permanganate results in the formation of a brown precipitate consisting mainly of manganese dioxide. However, it can easily be demonstrated that this precipitate is also an oxidant; addition of concentrated hydrochloric acid releases copious quantities of chlorine, and unreacted alkene is converted to the corresponding vicinal dichloride. At least part of this residual oxidant is likely manganate ion (MnO_4^{2-}) which, because it is a dianion, cannot be easily solubilized by phase transfer agents. Because of this it is often preferable to use aqueous permanganate as the source of oxidant. The precipitated manganate ion then dissolves in the water and disproportionates to permanganate and manganese dioxide.^{1b}

Experimental Section

Materials. Dimethyl polyethylene glycol was obtained as a mixture consisting of 1.5% dimethyl tetraethylene glycol, 9.0% dimethyl pentaethylene glycol, 12.5% dimethyl hexaethylene glycol, 15.9% dimethyl heptaethylene glycol, 16.4% dimethyl octaethylene glycol, 14.5% dimethyl nonaethylene glycol, 10.3% dimethyl decaethylene glycol, 5.8% dimethyl undecaethylene glycol, 2.8% dimethyl dodecaethylene glycol, 1.2% dimethyl tridecaethylene glycol, and 0.6% dimethyl tetradecaethylene glycol.¹² Adogen 464, a methyltrialkyl(C_8 - C_{10})ammonium chloride, was obtained from Ashland Chemicals. Dicyclohexano-18-crown-6 was obtained from the Aldrich Chemical Co. Cyclododecene was purified by a bromination-debromination procedure²¹ as follows. Commercially available cyclododecene (180 g, 1.08 mol) was dissolved in 200 mL of methylene chloride and placed in a 500-mL, three-necked, round-bottomed flask. The solution was stirred magnetically and bromine (170 g, 1.06 mol) was added dropwise until the color of the solution remained orange. The solution was warmed and stirred for a further 30 min, the solvent was removed by rotary evaporation, and the residue was distilled under vacuum [170 °C (1.5 mm)] to give 280 g (0.86 mol) of 1,2-dibromocyclododecene. The dibromide was dissolved in ether (150 mL) and acetic acid (15 mL) and stirred vigorously while two 10-g portions

of zinc dust were added. At this point the solution began to boil and an ice bath was raised into place during the addition of the remaining zinc (40 g). Water (50 mL) was added when the temperature of the solution began to drop, and the two layers were separated. The organic layer was washed with 2×100 mL of 10% HCl to remove zinc oxide and bromine and then by 2×100 mL of water. The solution was dried over anhydrous magnesium sulfate, concentrated on a flash evaporator, and distilled under vacuum [86–88 °C (4.5 mm)] to give 102 g (0.61 mol, 57%) of cyclododecene. Analysis of the product by GLC indicated it to be 60% trans and 40% cis. 1-Decene and trans-5-decene were obtained commercially (Aldrich) and used without further purification.

General Oxidation Procedures. A. Alkene (0.054 mol) was dissolved in 130 mL of solvent (methylene chloride or benzene) and 25 mL of acetic acid in a 500-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer. About 3 g of phase transfer agent (Adogen 464, dicyclohexano-18-crown-6, or dimethyl polyethylene glycol) dissolved in 20 mL of solvent was added, followed by powdered potassium permanganate (0.177 mol) in small portions during a period of 2 h. An ice bath was used to maintain the temperature below 30 °C. The mixture was then stirred vigorously overnight, cooled, and treated with 100 mL of water and 5 g of sodium bisulfite to reduce any excess oxidant. After 20 min the solution was acidified (concentrated HCl) and the manganese dioxide was reduced by addition, in small portions, of the required amount of sodium bisulfite. Any solid carboxylic acids which precipitated were collected by filtration, and the nonaqueous layer was separated. The aqueous layer was saturated with sodium chloride and extracted with 2×50 mL of ether. The combined organic layers were extracted with 2×100 mL of 5% of sodium hydroxide solution to remove any additional carboxylic acids, dried over anhydrous magnesium sulfate, and concentrated by rotary evaporation. The resulting yellow oil could then be analyzed directly by GLC (when benzene and dimethyl polyethylene glycol had been used as solvent and phase transfer agent) or distilled under vacuum and then analyzed.

The precipitated carboxylic acids were dissolved in a 5% sodium hydroxide solution and combined with the basic solutions from previous extractions. The solution was filtered to remove any residual manganese dioxide, acidified with concentrated hydrochloric acid, and extracted with 2×250 mL of ether. This solution was dried over magnesium sulfate and evaporated to give purified carboxylic acids. The yields obtained under various conditions are given in Tables I–III.

B. Alkene (0.054 mol) was dissolved in a mixture of methylene chloride (130 mL), acetic acid (25 mL), and water (100 mL) in a 500-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer. About 3.5 g of phase transfer agent (Adogen 464 or dimethyl polyethylene glycol) dissolved in 20 mL of methylene chloride was added. The mixture was cooled in an ice bath and powdered potassium permanganate (0.177 mol) was added in small portions over a 1-h period. The mixture was stirred vigorously for another 6 h, cooled, and treated with 5 g of sodium bisulfite to reduce any excess oxidant. After 20 min the solution was acidified (concentrated HCl) and the manganese dioxide reduced by addition, in small portions, of the required amount of sodium bisulfite. The products were then isolated as described above.

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Registry No.—1-Decene, 872-05-9; trans-5-decene, 7433-56-9; cyclododecene, 1501-82-2; dimethyl polyethylene glycol, 24991-55-7; potassium permanganate, 7722-64-7.

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Equilibration Studies: Amide-Imidate and Thioamide-Thioimide Functions

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Heats of methylation and vaporization have been determined for the following isomer pairs: *N,N*-dimethylbenzamide (1)-*N*-methyl-*O*-methylbenzimidate (2); *N,N*-dimethylacetamide (3)-*N*-methyl-*O*-methylacetimidate (4); and *N,N*-dimethylthioacetamide (5)-*N*-methyl-*S*-methylthioacetimidate (6). These enthalpies are used to calculate liquid- and gas-phase enthalpy differences for the isomer pairs: [ΔH°_l , ΔH°_g (kcal/mol)] -17.8 ± 1.8 , -16.6 ± 3.2 , 1-2; -17.0 ± 1.5 , -16.3 ± 2.5 , 3-4; -4.5 ± 0.7 , -2.7 ± 2.4 , 5-6. These values are used, in conjunction with earlier studies, to suggest that the gas-phase enthalpy difference between an unstrained dialkylamide and the corresponding dialkylimidate will be 15 ± 3 kcal/mol, and the enthalpy difference between a dialkylthioamide and the corresponding dialkylthioimide will be 2 ± 3 kcal/mol in favor of the amides. The enthalpy difference between an unstrained amide and its corresponding imidic acid isomer is estimated as 8 ± 3 kcal/mol in the vapor.

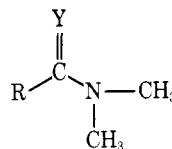
Gas-phase energy differences provide readily available fundamental data about chemical binding energies. This information can be useful in establishing relative chemical bond strengths and in testing energy predictions of current theory. Corresponding condensed-phase energy differences are important in understanding the effects of association and/or environment on molecular energies and in providing information about the prospective driving forces for chemical reactions.¹⁻⁴

Our continuing studies of energy differences between alkylmeric and protomeric isomers have been most extensive for amide-imidic acid derivatives. We now report that the gas- and liquid-phase enthalpy differences between the *N,N*-dimethylamide-*N*-methyl-*O*-methylimidate and *N,N*-dimethylthioamide-*N*-methyl-*O*-methylthioimide functions are unaffected by alkyl or aromatic substitution. This relative insensitivity to intramolecular environment, in conjunction with earlier data, suggests that parent systems provide useful guides to energy differences of alkylmeric isomers. This data also may be used to provide an estimate of the energy difference between parent amide-imidic acid systems.

Results

Heats of methylation and heats of vaporization were determined for the isomer pairs *N,N*-dimethylbenzamide (1)-*N*-methyl-*O*-methylbenzimidate (2), *N,N*-dimethylacetamide (3)-*N*-methyl-*O*-methylacetimidate (4), and *N,N*-dimethylthioacetamide (5)-*N*-methyl-*S*-methylthioacetimidate (6) (Table I). The differences in the heats of methylation give the differences in liquid-phase enthalpies for the isomer pairs (ΔH°_l , Table II).⁵ Inclusion of the differences in the heats of vaporization in a standard thermodynamic cycle gives the differences in the gas-phase enthalpies (ΔH°_g , Table II). In these cases, the differences in the heats of vaporization of each isomer and the resulting correction for the differential molecular environment in the condensed and vapor phases are not large. Apparently the intermolecular

forces in these liquids, unlike those in previous cases, are comparable for each isomer of the pair.^{2,6}



- 1, R = C₆H₅; Y = O
 3, R = CH₃; Y = O
 5, R = C₆H₅; Y = S

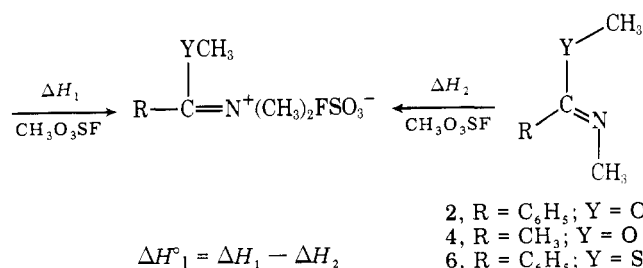


Table I. Enthalpies of Methylation and/or Vaporization for Methyltropic Isomers 1-6 (kcal/mol)

Compd	$\Delta H^\circ_{\text{meth}}^a$	$\Delta H^\circ_{\text{vap}}^b$
1	16.6 ± 1.2	14.8 ± 0.7
2	34.4 ± 0.6	13.6 ± 0.7^d
3	16.1 ± 0.7	10.9 ± 0.5^a
4	33.1 ± 0.8	10.2 ± 0.5
5	26.1 ± 0.2	17.6 ± 0.9
6	36.6 ± 0.3	6.0 ± 0.2^c 15.8 ± 0.8

^a The estimated error is 5% (see ref 1 for discussion) for 3 runs in each case. ^b The error is the standard deviation. ^c The heat of fusion. ^d In kcal/mL.