doublet at τ 8.1 with J_{PCH} = 13 cps and multiplets at τ 2.15 and 2.52 with the expected integration.

Anal. Calcd for $C_8H_{11}PS$: C, 56.44; H, 6.52. Found: C, 56.28; H, 6.60.

Sodium Dimethyldithiophosphinate. Tetramethylbiphosphine disulfide was treated with an equimolar amount of SO_2Cl_2 to give dimethylthiophosphinyl chloride,[34] bp 50–55° (3 mm) [lit.[34] 82–83° (16 mm)]. The acid chloride was treated with sodium hydrogen sulfide[35] and the sodium salt of the dithio acid recrystallized from benzene–ethanol. The infrared spectrum shows bands at 3300–3400, 1619, 1400 and 1272, 937, 905, 731, and 717 cm^{-1}. The nmr spectrum in D_2O exhibits a doublet at τ 8.01 with J_{PCH} = 13 cps (standard = $(CH_3)_3Si(CH_2)_3SO_3Na$). The preparation of dimethylphosphinic acid has been described.[13]

Measurement of p*K*'s. The solutions were made up as previously described[13] at a concentration of $\sim 10^{-1}$ *M* for both standard and substrate.

Chemical shifts (Δ) were plotted against H_0 (Figure 1) to give approximate p*K* and *M* values according to eq 2. The approximate p*K* can be obtained from the H_0 value at $^1/_2(\Delta_B - \Delta_{BH^+})$. The approximate *M* value can be obtained graphically or by solution of eq 2 at some point other than $H_0 = pK_{BH^+}$. Values of Δ_B and Δ_{BH^+} were then obtained from the smoothed curve of Δ *vs.* H_0: Δ_B is the Δ at H_0 (0.5% protonation) = $pK_{BH^+} - 2.3/M$, Δ_{BH^+} is the Δ at H_0 (99.5% protonation) = $pK_{BH^+} + 2.3/M$. A least-squares analysis of the data was then done using eq 2 and points between 5 and 95% protonation, *i.e.*, between $H_0 = pK \pm (1.3/M)$.

Acknowledgment. The nmr spectrometer used in this work was purchased with funds from the National Science Foundation. Sigma R. Alpha prepared the dimethyl methylphosphonate.

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(35) T. A. Mastryukova, A. E. Shipov, and M. E. Kabachnik, *Zh. Obshch. Khim.*, 31, 507 (1961); *Chem. Abstr.*, 55, 22101 (1961).

Comparison of Liquid-Phase and Gas-Phase Reactions of Free Radicals[1]

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Abstract: The theoretical and practical effects of gas–liquid phase change on rates and products of free radical reactions are discussed, mostly in terms of ratios of rate constant for competing reactions. Effects of free volumes, concentration changes, solvent cages, and third bodies are now fairly well understood, but when enough competing reactions are involved, the effect of phase change may become complicated. Previous work provides several examples where phase change has, or has not, affected competing free radical reactions and several instances where solvent change has affected competitions. The present survey now suggests that solvation effects are widespread in free radical reactions but often obscured by the necessity of studying them in competing reactions. Solvation effects in the most inert solvents appear to be as far from gas-phase results as they are from solvation effects in the most polar solvents. Thus, comparisons of gas-phase and liquid-phase reactions of free radicals are important in any absolute measure of solvation effects.

During the development of free radical chemistry, the organic and polymer chemists have been concerned mostly with liquid-phase reactions, while physical chemists have been concerned mostly with gas-phase reactions. There has been little effort to correlate the work of the two groups. As considerable data have accumulated on each phase, with little overlap, several related questions arise. To what extent can we predict rates or products in one phase from data in the other? Is there any discernible change in rate constants with phase change? Why do some reactions proceed in both phases while others proceed only in one? Which phase should be chosen for preparative purposes? The object of this paper is to consider some reactions for which data on both phases are available, to deduce some generalizations, and to point out remaining problems. The next two portions of this section consider some theoretical aspects of phase changes, then some generalities about free radical reactions. The following section then reviews experimental data. Conclusions are summarized in the last section.

Theoretical Aspects of Phase Changes. One interesting aspect of phase change is the free-volume effect. When we assume that the activities of the reactants and the activated complex are measured by their vapor pressures and that attractive forces with other molecules are negligible, the partial pressure of each reactant is given by

$$p(v - b) = nRT$$

Here $v - b$ is the corrected volume in the van der Waals equation, corresponding roughly to the free volume of the container not occupied by molecules. When we go from (say) 0.01 *M* reactant in the gas phase to a 0.01 *M* solution in benzene at 50°, $v - b$ changes from about 999.7 ml/l. to about 250 ml/l. (assuming that there is no free volume in benzene at 0°K) and the vapor pressure of the reactant, in the absence of all interactions with the solvent, is increased fourfold. We neither find nor expect phase change to have much effect on rates of first-order reactions: although the vapor pressure of the reactant (in the liquid phase) is four times as great, the reactant is present in only one-fourth of the volume. However, for a second-order reaction, the product of the vapor pressures of the reactants is increased 16-fold while the volume is decreased only fourfold, and the

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(1) This paper extends one presented to the Division of Organic Chemistry at the Symposium on Reactions of Free Radicals at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 7, 1965, and subsequently to the Colorado, California, and Santa Clara Valley Sections.

rate of reaction per unit volume should be four times as great. For a third-order reaction, the factor should be 16.

More elegant treatments come to similar conclusions. Benson[2a] concludes that a reaction will go fastest in the medium which favors the association of reactants and estimates that a bimolecular reaction might be 20 times as fast in solution as in the gas phase. The collision theory of reaction rates suggests that there should be two to three times as many collisions between a particular pair of molecules in solution as in the gas phase and that, for the same activation energy, the rate will be correspondingly higher.[3] The absolute rate theory, from considerations of entropies of activation, leads to the same final result.[3]

At low pressures, the rates of some gas-phase reactions become smaller than expected from rates at higher pressures or in the liquid phase. In unimolecular reactions, first-order rate constants begin to fall off at pressures which are insufficient to maintain an equilibrium concentration of activated reactant molecules. These pressures range roughly from a fraction of a millimeter of mercury for molecules with 6 or more atoms to some hundreds of millimeters for molecules with 3 or fewer atoms.[2c] In combinations of two atoms or small free radicals, the heat of reaction is sufficient to cause immediate separation unless some of this heat can be removed by collision with a third body. Thus, combinations of atoms normally require a third body (are termolecular) but bimolecular reactions of radicals become less dependent on pressure as the complexity of the radical and the opportunities for internal dissipation of the heat of reaction increase.[2d]

Before we examine data on rates of free radical reactions, and since the transition-state theory treats a rate as an equilibrium, let us see what phase change does to an easily measured and uncomplicated equilibrium constant. Table I gives the equilibrium constants for the dissociation of N_2O_4 in the gas phase and in several solvents.[4]

Table I. Equilibrium Constants[4] for $N_2O_4 \rightleftarrows 2NO_2\cdot$ at 20°

Solvent	K, M	$\Delta H_c°$,[a] kcal/mole
Gas phase	382	13.7
$SiCl_4$	17.8	20.5
CS_2	13.3	19.4
CCl_4	8.05	18.8
$CHCl_3$	5.53	21.2
EtBr	4.79	20.5
C_6H_5Br, C_6H_5Cl	3.7	19.4
C_6H_6	2.23	22.2

[a] Dissociations are endothermic.

From the free-volume aspect, the effect of phase change has the direction expected and is greater than expected; there is much less dissociation in solution. However, the effect of solvent change on the equilibrium constant is about one-third as large as the effect of phase change. Further, the heats of dissociation vary erratically among the solvents and the spread is almost as great as between gas phase and carbon tetrachloride solution. The lack of correlation between K's and ΔH's shows that changes in entropies of solution largely compensate for changes in enthalpy terms.

Table II shows that the same considerations apply in reaction rates as in the equilibria above. Rate constants for the dimerization of cyclopentadiene in various media at 50° are listed in order of decreasing rate constants.[2b] Although the rate constants differ by a factor of only 3 (0.5 log unit), the erratic but compensating variations in frequency factors (40-fold) and in activation energies (2.7 kcal/mole) again suggest important interactions of reactants and solvents.

Table II. Solvent Effects in the Dimerization of Cyclopentadiene[2b] at 50°

Solvent	$-\log k$	$\log A$	E, kcal/mole
Gas phase	5.2	6.1	16.7
CS_2	5.2	6.2	16.9
Cyclopentadiene	5.2	5.8	16.2
AcOH	5.0	5.0	14.7
C_6H_6	5.0	6.1	16.4
CCl_4	4.9	6.7	17.1
EtOH	4.7	6.4	16.4
$C_6H_5NO_2$	4.7	5.5	15.1
Paraffin	4.7	7.1	17.4

The examples above show that the effects of solvent molecules on reacting solutes, whether they be complexing, solvation, or restriction of motion, and even with nonradical, nonpolar, nonhydrogen-bonding materials, are usually about as large as, and sometimes much larger than, effects due to free volume or frequency of collision.

Free Radical Reactions. Table III classifies reactions of free radicals. Free radicals are commonly produced in pairs by decompositions of peroxides or azo compounds (reaction −1). They interact and destroy each other in pairs by reactions 1 (combination) or 2 (disporportionation). Both reactions 1 and 2 cannot be avoided, and if these were the only reactions of free radicals, they would be of little interst. The interest arises from the other reactions which compete with reactions 1 and 2 and with each other. Reaction 3, usually the abstraction of a hydrogen or halogen atom (chain transfer in polymerization), is the most important and most studied reaction of free radicals. Reaction 4, the addition of an atom or radical to a double or triple bond (or to oxygen), is an essential step in the free radical additions of many reagents to unsaturated compounds, usually in combination with reaction 3. Scission, reaction −4, is the reverse of 4, and is illustrated by the loss of ethylene units from an alkyl radical and by the scission of *t*-butoxy to acetone and methyl. Reaction 5, rearrangement, corresponds to internal (unimolecular) abstraction or to other shifts of atoms or groups within radicals.

Of the eight listed reactions of free radicals in Table III, dissociation (−1), diffusion from cage (D), scission (−4), and rearrangement (5) are first-order reactions; the rest are bimolecular; occasionally 4 is termolecular. Reaction conditions are usually chosen to limit the

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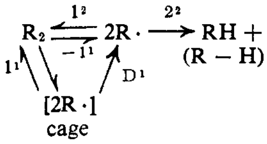
(2) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960: (a) p 504; (b) p 509, data compiled by A. Wasserman; (c) p 234; (d) p 308.

(3) K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 201.

(4) E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," 2nd ed, Oxford, 1947, p 184, from data of Cundall.

Table III. Reactions of Free Radicals

No.	Type	Example (superscript indicates kinetic order)
-1^1	Dissociation	
1^2	Combination	
2^2	Disproportionation	
D^1	Diffusion from cage	
3^2	Abstraction, transfer	$R\cdot + XY \xrightarrow{3^2} RX + Y\cdot$
$4^{2(\text{or } 3)}$	Addition	$R\cdot + A{=}B \underset{-4^1}{\overset{4^2}{\rightleftarrows}} RAB\cdot$
-4^1	Scission	
5^1	Rearrangement	$R\cdot \xrightarrow{5^1} R'\cdot$

important competing reactions to two or three. Rates, yields, or kinetic chain lengths commonly measure the competition between chain-terminating reactions 1 and 2 and chain propagations 3 and/or 4, as in halogenation, oxidation, polymerization, or telomerization. For long kinetic chains the competition between two reactions of types 3 and 4, or the competition of one of these with another of the reactions 3, 4, −4, or 5, may be measured by ratios of reaction products; reactions 1 and 2 and rate data can then be neglected. Thus both rate and product studies give us ratios of rate constants, and we need ratios of rate constants to predict rates or products. This paper will deal only with the effects of phase change on ratios of rate constants in free radical reactions, because ratios are the only bases available. Measurements of absolute rate constants require measurements of the very low concentrations of reactive radicals. Although such data are accumulating slowly, I know of no case where the absolute rate constants are available for the same reaction in both gas and liquid phases. If we had one set, we would still need another set to get ratios and to compare experimental results.

In considering the effects of phase change on these competitions, we should note that the effect of phase change on concentration can be very large. Thus the concentration of a pure organic liquid is about 10 *M*, while the concentration of a gas at standard conditions is only about 0.05 *M*. At 30-mm pressure and 200°, where many gas-phase reactions have been studied, the concentration of gas is only 0.001 *M*. Apart from any effect of phase change on equilibrium constant, normal concentration effects in phase change will favor dissociation in the gas phase (reactions −1 and −4), and association in solution (reactions 1 and 4).

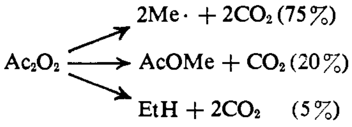
Review of Experimental Data

Phase change usually has little effect on ratios of rate constants. In the following discussion, emphasis is on the exceptions and on instances where concentration changes produce notable changes in results.

Unimolecular Decomposition to Product Radicals (Reaction −1). In decompositions of peroxides or azo compounds to give free radicals, we are concerned with the production of radicals, not with their reactions. Absolute rate constants are available; they show that the effect of phase change is small.

Raley, Rust, and Vaughan[5] measured the first-order rate constants for decomposition of di-*t*-butyl peroxide in the gas phase and in cumene, *t*-butylbenzene, and tributylamine as solvents. The vapor phase k_1 was about 75% as large as the k_1 in the three solvents. The solvent k_1 tended to decrease with the concentration of peroxide, an indication of induced decomposition. Apparently, the effect of phase change on k_1 is less than the effect of any induced decomposition. Here it would be useful to have some solution measurements at concentrations as low as those used in the gas-phase studies. Smid, Rembaum, and Szwarc[6] carried out similar studies with dipropionyl peroxide and dibutyryl peroxide. The first-order rate constants in dilute solutions in isooctane and *n*-hexane were close to those in the gas phase. They were 50–100% greater in benzene and toluene and still larger in polar solvents. Thus, the difference between the nonpolar solvents and the gas phase is less than the differences among solvents.

Cage Effects (Reactions 1 and D). When two radicals are formed very close together in solution (−1), the competition between their very fast combination (1) and their diffusion apart (D) affects the products of reaction. These competitions are normally important only in solution. Herk, Feld, and Szwarc[7] generated methyl radicals by the decomposition of acetyl peroxide in the gas phase and in isooctane solution at 65°. In isooctane, the products were



$$Ac_2O_2 \longrightarrow \begin{cases} 2Me\cdot + 2CO_2\,(75\%) \\ AcOMe + CO_2\,(20\%) \\ EtH + 2CO_2 \quad (5\%) \end{cases}$$

Carrying out the reaction in the presence of styrene resulted in scavenging of free methyl radicals but did not affect the yields of methyl acetate or ethane. These are therefore nonradical or cage products, formed so rapidly that the solvent or scavenger cannot intervene. In the gas phase, the intermediate radicals separated at once and no methyl acetate was formed; it is therefore a cage product. More ethane was formed in the gas phase, but since this was largely eliminated by the addition of iodine, it is clear that ethane arises from diffusing methyl radicals in the gas phase but is mostly a cage product in solution. Recent work shows how cage recombination of radicals from acetyl peroxide leads to slightly lower rate constants for decomposition[8a] than in the gas phase, especially in solvents of higher viscosity.[8b]

Herk and co-workers[7] found a much larger cage effect in the photodecomposition of azomethane in isooctane solution. Under conditions where only 6% of the methyl radicals from acetyl peroxide combined to give ethane, 65% of the methyl radicals from azomethane gave ethane. The ethane practically disappeared from the gas-phase decomposition of azomethane.

Lyon and Levy[9] have reported an interesting comparison of the gas-phase and liquid-phase decompositions of azomethane according to the procedure of Herk, Feld, and Szwarc. They decomposed mixtures of azomethane and hexadeuterioazomethane. In the gas phase there was statistical combination of methyl and deuteriomethyl radicals to form ethane. In solution, all the ethane found was either hexadeuterated or undeuterated. Lyon[10] showed also that a liquid phase

(5) J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1336 (1948).

(6) J. Smid, A. Rembaum, and M. Szwarc, *ibid.*, **78**, 3315 (1956).

(7) L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961).

(8) (a) J. W. Taylor and J. C. Martin, *ibid.*, **88**, 3650 (1966); (b) W. Braun, L. Rajenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

(9) R. K. Lyon and D. H. Levy, *J. Am. Chem. Soc.*, **83**, 4290 (1961).

(10) R. K. Lyon, *ibid.*, **86**, 1907 (1964).

is not necessary for a cage effect; it can be demonstrated also at high pressures of gases. In the photolysis of azomethane in propane at 98° at pressures up to 50 atm, as the densities of the mixtures increased from 0.087 to 0.260 g/cc, the ethane:methane ratio increased from 0.063 to 0.10. This increase in ethane shows that more propane does not supply more hydrogen atoms to methyl radicals as much as it favors their cage combination. All of the ethane was formed in the cage.

Combination and Disproportionation of Radicals (Reactions 1 and 2). Here both competing reaction are second order and involve the same reactants. The effects of phase change are small.

Dixon, Stefani, and Szwarc[11] measured the combination and disproportionation of ethyl radicals formed in the photolysis of diazoethane. The ratio of these rate constants was measured by the ratio of ethylene plus ethane to butane. In the gas phase, k_2/k_1 increased from 0.12 at +40° to 0.16 at −65°, independent of pressure (hence combination of two ethyl radicals does not require a third body below 40°). In isooctane, the same ratio increased from 0.15 at 85° to 0.34 at −191°. Thus the competition between disproportionation and combination depends more on temperature than it does on reaction medium. These authors think that both reactions involve similar transition states, disproportionation being slightly favored by low temperatures and solvent cages.

Interactions of Alkylperoxy Radicals. The group at the Shell Development Co.[12] was the first to suggest that interaction of alkylperoxy radicals produces alkoxy radicals. It now appears that these reactions take place through decomposition of an unstable intermediate tetroxide.[13] Decomposition of this intermediate produces caged alkoxy radicals in solution (apparently subject to the viscosity of the solvent[14]) but not in the gas phase. Further, secondary and tertiary alkylperoxy and alkoxy radicals behave very differently. Since these reactions are still under investigation, discussion is deferred. However, these efficiencies of chain termination are important in determining kinetic chain lengths in oxidations of alkanes (see below) and in induced decompositions of hydroperoxides; phase changes are important because of cage effects.

Bimolecular Abstractions of Hydrogen or Halogen (Reaction 3). Hass, McBee, and Weber[15] made a classic study of the relative reactivities of primary, secondary, and tertiary carbon–hydrogen bonds toward chlorine atoms in the chlorination of isopentane. Some of their experiments, carried out in both liquid and gas phases over a wide range of temperatures, are summarized in Table IV. In either phase the relative reactivities of primary, secondary, and tertiary hydrogen atoms approach unity with increasing temperature but the selectivity is lower in the liquid phase. Selectivity in the liquid phase at 100° corresponds to the low selectivity in the gas phase at 600°. The best explanation that I know for this phase difference is the following. The chlorine atom in solution is so reactive and its lifetime is so short that its reactions depend on the statistics of a series of cage encounters ("cage effect") as well as on the relative reactivities of the surrounding carbon–hydrogen bonds involved. It should follow that this liquid-phase–gas-phase difference will disappear as the attacking radicals become less reactive and their lifetimes become long compared with the times required for diffusion.

Table IV. Relative Rates of Reaction of C–H Bonds with Chlorine Atoms[15]

	Temp, °C	Tertiary	Secondary	Primary
Liquid phase	−60	13	8.5	1.00
	100	3	2	1.00
Gas phase	300	4.43	3.25	1.00
	600	3.5	2.2	1.00

This work has recently been corroborated and extended by Tedder and co-workers.[16] In the gas-phase chlorination of *n*-hexane[16a] in excess nitrogen at 40–212°, the relative reactivity of the total secondary and primary hydrogen atoms is $k_s/k_p = (2.2 \pm 0.6) \exp[(214 \pm 127)/RT]$. In a solution containing carbon tetrachloride, the corresponding relation for −70 to +39° is $k_s/k_p = (0.8 \pm 0.2) \exp[(597 \pm 20)/RT]$.

To the extent that these frequency factors and activation energies are reliable, the greater selectivity of the gas-phase chlorination at 39–40° ($k_s/k_p = 3.11$ *vs.* 2.14) is due mostly to the ratios of the A factors (2.74 times as great in the gas) but largely offset by the activation energy term (0.54 times as great at 40° in the gas). These authors conclude that the effect of phase change on the ratios of the A factors is probably associated with the cage effect, but that the differences in the activation energies are probably associated with solvation of chlorine atoms in solution, even in the least polar solvents. (For a simple cage effect, selectivities should become more similar at increasing temperatures; instead, they diverge.)

They also compared reactivities in chlorination of various C–H bonds in normal acid chlorides and fluorides of 5–7 carbon atoms.[16b] They find that, in the gas phase, the acid halide group has no effect on reactivity of C–H bonds beyond the β-carbon atom, but in the liquid phase the effect of that group is readily detected at separations even of three additional carbon atoms. The effect of phase change is attributed to solvation in the transition state of the hydrogen chloride being formed.

When these results are compared with those of Russell and Walling[17] on complexing solvents in chlorination, their "noncomplexing solvents" (alkanes and carbon tetrachloride) must instead be weakly complexing solvents in comparison with benzene derivatives and carbon disulfide.[16a] Apparently, enough solvation to affect k_s/k_p by a factor of about 2 cannot be avoided in solution chlorinations.

No effect of phase change has appeared in competing abstraction reactions of methyl radicals, perhaps because they are less polar and less susceptible to solvation than reactions of chlorine atoms. Trotman-

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(15) H. B. Hass, E. T. McBee, and P. Weber, *Ind. Eng. Chem.*, **28**, 333 (1936).

(16) (a) I. Galiba, J. M. Tedder, and J. C. Mattou, *J. Chem. Soc., Sect. B*, 604 (1966); (b) H. Singh and J. M. Tedder, *ibid.*, 605 (1966).

(17) E. S. Huyser, "Advances in Free Radical Chemistry," Vol. 1, G. H. Williams, Ed., Academic Press Inc., New York, N. Y., 1965, p 77.

Dickenson[18] has measured the absolute rate constants for abstraction reactions of methyl radicals with various hydrocarbons in the gas phase at 100° by comparing these rates with those for combinations of methyl radicals. Edwards and Mayo[19] have measured the relative rates of abstraction reactions of methyl radicals, generated by decomposition of acetyl peroxide, with carbon tetrachloride and with hydrocarbons, all in solution at the same temperature. Table V shows that the relative reactivities of several kinds of carbon–hydrogen bonds in the two phases as measured by the two methods are nearly identical. The agreement also shows that phase change does not affect the competition between the bimolecular combination and abstractions.

Table V. Relative Rates of Reaction of C–H Bonds with Methyl Radicals at 100°

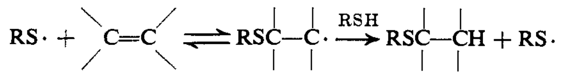
Compd	k_{RH}, gas[18] at 100° $\times 10^6$	$\frac{k_{RH}}{k_{CCl_4}}$, soln[19] at 100°	$\frac{k_{RH}\ (\text{gas})}{k_{RH}/k_{CCl_4}\ (\text{soln})}$
Benzene[a]	0.091	0.04	2.3
Acetone	1.0	0.40	2.5
Toluene	1.9	0.75	2.5
1-Octene	7.7	3.2	2.4
Cyclohexane	3.4	4.5[b]	0.8[b]

[a] It now appears that methyl radicals do not abstract hydrogen directly from benzene but by a more complex process. [b] The discrepancy with cyclohexane is accounted for by the suggestion of DeTar and Wells[20] that the chain chlorination of cyclohexane by carbon tetrachloride depleted the concentration of carbon tetrachloride in the solution experiment.

Additions of Free Radicals to Multiple Bonds (Reactions 4 and −4). Additions of free radicals to oxygen or unsaturated compounds (4) are usually both exothermic and reversible; the reverse reaction is scission or cracking (−4). As in combinations of two radicals (1), when the radicals and molecules are small, a third body is needed to prevent immediate dissociation, as in reaction of methyl radicals with oxygen, a third-order reaction.

The importance of reversibility, even in the liquid phase below 100°, is demonstrated by the isomerization of *cis* to *trans* isomers by bromine atoms[21] and thiyl radicals,[22] and by ceiling temperatures in vinyl polymerization.[23] Mass action and enthalpy effects favor additions at higher concentrations and at lower temperatures; entropy effects favor scission in the gas phase at high temperatures. Benson[24] has recently calculated the effects of oxygen pressure and temperature on the fractional conversion of various alkyl radicals to the corresponding alkylperoxy radicals. His paper also shows the effects of changes in resonance stabilization of the initial and final radical on the balance between addition and scission.

Sivertz and co-workers have measured rates of additions of mercaptans to alkenes in the gas phase[25] and in benzene solution.[26] They report that over-all rates in the gas phase have a negative temperature coefficient which they attribute to the reversible addition of RS· radicals ("complex formation")



$$RS\cdot + \gt C{=}C\lt \rightleftharpoons RS\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \xrightarrow{RSH} RS\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}H + RS\cdot$$

In benzene solutions, the over-all activation energies are positive but small; reversibility at normal concentrations is less important. Data are inadequate to tell much more about the effect of phase change. The gas-phase addition of hydrogen bromide to propylene[25] also has a negative temperature coefficient.

Competition between Abstraction and Addition (Reactions 3 and 4). Abstraction and addition reactions of free radicals often compete. Since only the addition reaction is immediately reversible, both concentration and temperature may affect comparison of gas-phase and liquid-phase reactions. From a 10% solution of chlorine and toluene at 0° in the dark, Kharasch and Berkman[27] found that 55% of the chlorine reacted by substitution in the side chain and 45% by addition to the benzene ring. On the other hand, the gas-phase chlorination of toluene would give only benzyl chloride. In solution, the addition of a chlorine atom to the benzene ring is readily followed by reaction with another chlorine molecule and completion of addition. However, at the lower concentrations and higher temperatures used in gas-phase reactions, the concentration of the free radical formed by addition of the chlorine atom is inadequate to support much addition. The irreversible displacement of a side-chain hydrogen atom is therefore the dominant reaction, and the observed product is benzyl chloride.

The chlorination of an alkene may occur by addition to the double bond to give a dichloride or by hydrogen abstraction to give an allylic chloride. In the gas-phase free radical reaction,[28] addition predominates at low temperatures and is replaced by allylic substitution at high temperatures. This shift seems to be due mostly to the reversibility of the addition of chlorine atoms to alkenes at high temperatures. In the liquid phase, the results are complicated by the intrusion of an ionic reaction. Thus, Burgin and co-workers[29] report that pure isobutylene and chlorine do not react in the gas phase in the dark below 150°. However, as soon as a liquid film appears at lower temperatures, methallyl chloride is formed very rapidly. This reaction is not affected by the presence of oxygen, which inhibits free radical chlorinations. Poutsma[30] has recently and ably extended this work. In the liquid phase most alkenes chlorinate by two mechanisms, one free radical and oxygen inhibited, the other ionic and not affected

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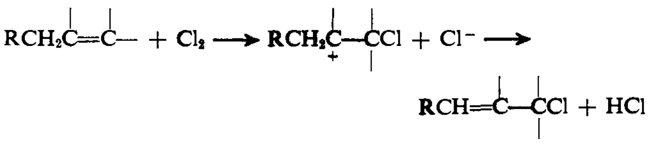
by oxygen. The ionic reaction gives mostly allyl substitution.



$$RCH_2\overset{|}{C}{=}\overset{|}{C}- + Cl_2 \longrightarrow RCH_2\underset{+}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}Cl + Cl^- \longrightarrow RCH{=}\overset{|}{C}-\underset{|}{\overset{|}{C}}Cl + HCl$$

The free radical chlorination gives both addition and substitution products, depending on the alkene. Here phase change greatly affects the course of a chlorination because a competing polar reaction, requiring solvation of ions, is possible only in the liquid phase.

The examples below describe abstraction and addition reactions of phenyl radicals with toluene and show that phase change has little effect on other abstraction–addition competitions when the addition is not reversible.

Jacquis and Szwarc[31] discussed the effect of phase change on reactions of phenyl radicals with toluene. In solution, the reaction of phenyl radicals with toluene had been reported to produce only methylbiphenyls, not bibenzyl. However, in the gas phase above 600°, phenyl radicals react with toluene to give benzene and benzyl radicals; the principal product is bibenzyl. Only with the higher concentrations and lower temperatures usually associated with solutions is the concentration of the addition product of the phenyl radical to the benzene ring high enough for a hydrogen atom to be abstracted and for the reaction to be completed.

More recent work in solution has given better measures of the addition/abstraction ratio for reaction of phenyl radicals with toluene. For 80°, Hey [32] gives 6.7. For 60°, the data of Pryor, *et al.*,[33] give 1.14. The apparent effect of temperature here is the opposite of that expected, but the results were obtained by different techniques. If scission of the phenyl radical–toluene adduct is fast enough, the addition/abstraction ratio is proportional to the concentration of phenyl radicals. Quantitative extensions of such work to both phases would be of interest. The addition/abstraction ratio is already known[32,33] to depend on substitution in the phenyl radical.

However, where the addition reaction is irreversible, the effect of phase change on the addition–abstraction competition is small. Szwarc and co-workers have measured the relative rates of reaction of trifluoromethyl radicals with 2,3-dimethylbutane (by hydrogen abstraction, k_3) and with a series of vinyl compounds (by addition, k_4) in both the gas phase[34] and the liquid phase.[35] Differences in activation energies and frequency factors were measured in the gas phase from 65 to 180° and in the liquid phase from 0 to 95°. The gas-phase reactivities of the alkenes, measured by k_4/k_3 at 65°, increase 200-fold when the least reactive, vinyl fluoride, is compared with the most reactive, 2,3-dimethyl-1,3-butadiene. This increase is due to a decrease in $E_4 - E_3$; the A_4/A_3 factors remain essentially constant. In the liquid phase[35] the values of $E_4 - E_3$ are substantially the same as in the gas phase. The k_4/k_3 and the A_4/A_3 ratios tended to be 20–30% larger on the average than the corresponding gas-phase values. In an earlier paper,[36] this phase difference was attributed to some lag in stabilization of the adduct in the gas phase. In this case, where addition is irreversible, phase change and the low free volume of the liquid affect the addition and abstraction reactions to about the same extent.

Jaacks and Mayo[37] studied the di-*t*-butyl peroxide initiated telomerization of ethylene and carbon tetrachloride at 140°, in the liquid phase in three solvents, and in the gas phase at total pressures of $^1/_3$–28 atm. The objective was to determine the effects of solvent change and phase change on the variation with n of the transfer constants of the radicals $Cl_3C(C_2H_4)_n\cdot$. The transfer constants, C_n, are defined as (rate constant for chlorine abstraction from CCl_4 by $Cl_3C(C_2H_4)_n\cdot$)/(rate constant for addition of the same radical to ethylene); they measure directly the competition between reactions 3 and 4 of ω-trichloroalkyl radicals. These transfer constants were known to change about 40-fold as n increased from 1 to 4 in the liquid phase at 70°. Since this effect seems to be due to increasing separation of the trichloromethyl group from the free valence in the growing polyethylene radical, effects of both solvent change and phase change were expected. At 140°, the effect of changing the solvent from *n*-octane to methanol hardly exceeded 30%. When the results in octane and at 1.2 atm in the gas phase are compared, the values of C_1 are nearly identical and the indicated value of C_4 in the gas phase is about twice the octane value. While the results for C_2 and C_3 are subject to more experimental error, phase change only exaggerates slightly the very large drift in C_n with increasing n.

Competition between Chain Propagation (3 and 4) and Termination Reactions (1 and 2). If propagation is fast enough, chain reactions can proceed nearly as well in normal low gas-phase concentrations as in the liquid phase. One example is the free radical chlorinations above. Another is the free radical addition of hydrogen bromide to double bonds.[38,39] On the other hand, while the photochemical addition of hydrogen sulfide to 1-butene would proceed readily in the liquid phase at 0 or −78°, reaction under ultraviolet illumination in the gase phase at room temperature at a total pressure of 300 mm was very slow.[40] At this low concentration of reactants, one of the propagation steps was unable to compete with chain termination. These relations are complicated by the reversibility of the addition reaction and by the negative temperature coefficient of the over-all addition reactions in the gas phase.[25]

A similar situation arises in autoxidations. Although many initiated autoxidations proceed readily at or below 100° in the liquid phase, gas-phase reactions of similar chain lengths require temperatures of 200° or more at pressures of about 1 atm. This difference is largely an effect of reactant concentration on the competition between chain propagation and termination reactions. Although the initiated oxidation of isobutane gives chain lengths of only about one at a total pressure below 1 atm at 150°, much longer chains can be obtained at superatmospheric pressures (see below).

Competition between Abstraction (3) or Addition (4) and Rearrangement Reactions (5). My discussion of the change in transfer constant with chain length in the telomerization of ethylene and carbon tetrachloride oversimplified the situation. In the liquid-phase reaction, kinetic chains are very long and only normal telomers are obtained. In the gas phase at 1 atm where the total concentration of reactants is only about 0.03 *M*, only 20–30% of the products obtained are normal telomers; the remaining 70–80% are isomers of normal telomers,[37] arising by rearrangements reactions such as

$$Cl_3CCH_2CH_2CH_2CH_2\cdot \longrightarrow \cdot CCl_2CH_2CH_2CH_2CH_2Cl$$

$$Cl_3CCH_2CH_2CH_2CH_2CH_2CH_2\cdot \longrightarrow Cl_3CCH_2\dot{C}HCH_2CH_2CH_2CH_3$$

The rearrangements of the indicated radicals compete with both addition to ethylene (4) and abstraction from

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carbon tetrachloride (3). The indicated products continue to react with ethylene and/or carbon tetrachloride to give telomer isomers. These rearrangements are due more to a concentration effect than to a phase change. As the concentrations of ethylene and carbon tetrachloride decrease, unimolecular rearrangements such as those above replace the normal bimolecular addition and displacement reactions. These rearrangements become less important at higher pressures in the gas phase. Such rearrangements become of increasing importance in solution in unreactive solvents.[41]

Competition between Abstraction and Scission (Reactions 3 and −4). Walling and co-workers have examined in detail the competition between the reactions

$$t\text{-BuO}\cdot + \text{RH} \xrightarrow{k_a} t\text{-BuOH} + \text{R}\cdot$$

$$t\text{-BuO}\cdot \xrightarrow{k_d} \text{AcMe} + \text{Me}\cdot$$

in chain decompositions of *t*-butyl hypochlorite where the fast complementary step is

$$\text{R}\cdot\ (\text{or Me}\cdot) + t\text{-BuOCl} \longrightarrow \text{RCl (or MeCl)} + t\text{-BuO}\cdot$$

Of special interest here are their measurements[42] of k_a/k_d at 5:1 ratios of cyclohexane and *t*-BuOCl in the gas phase, in several solvents, and at several temperatures. Some of their results are summarized in Table VI. Each k_a/k_d ratio represents the slope of a (linear) plot of *t*-BuOH/AcMe found against the concentration of cyclohexane in the gas phase or in the chosen solvent. Solvents are arranged in order of decreasing values k_a/k_d.

Table VI. Solvent Effects[42] on Reactions of *t*-Butoxy Radicals at 40°

Solvent	k_a/k_d	$E_d - E_a$	log A_a/A_d
Gas phase	584	10.56	−4.61
$Cl_2FC–CF_2Cl$	52.8	9.65	−5.04
C_2Cl_4	39	8.72	−4.49
C_6H_5Br	25.4	8.17	−4.34
C_6H_6	24.7	8.66	−4.63
m-$C_6H_4Cl_2$	24.3	8.40	−4.49
C_6H_5F	22.4	7.85	−4.15
o-$C_6H_4Cl_2$	19.2	8.14	−4.43
C_6H_5CN	16.9	8.28	−4.58
C_6H_5Cl	16.4	7.21	−3.82
C_2HCl_3	14.2	7.34	−3.99
trans-$C_2H_2Cl_2$	14.2	7.69	−4.16
cis-$C_2H_2Cl_2$	9.1	7.04	−3.92
MeCN	8.1	9.54	−5.73
AcOH	2.9	5.95	−3.66

In the gas phase, bimolecular hydrogen abstraction is favored over unimolecular decomposition by a factor of at least 10 in comparison with the liquid phase. Considerations of free volume or collision frequency predict a shift in the *opposite* direction. Thus, even in the most inert fluorocarbon solvent, solvation or cage effects far outweigh any effect of phase change expected from a noninteracting solvent. Among different solvents at 40°, k_a/k_d varies by a factor of up to 18. The differences in activation energies are erratic but mostly compensated by changes in ratios of A factors. Although neither changes in $E_d - E_a$ nor in log (A_a/A_d) parallel those in k_a/k_d, changes in these factors mostly compensate each other, as in the equilibrium and nonradical reactions in the introductory section.

The effect of phase change on k_a/k_d is the largest one I know about in free radical reactions. Apparently solvation or complexing favors the unimolecular cleavage over the bimolecular hydrogen abstraction, but we cannot tell whether complexing promotes or hinders both competing reactions.

Competition between Abstraction (3), Cleavage (−4), and Termination Reactions (1 and 2). My last example deals with the oxidation of isobutane[43] in gas and liquid phases at 100–150°. This example shows how the competition of several reactions, each affected in a simple way by concentration changes with phase change, can affect both products and apparent rate constants. Table VII gives the liquid-phase products and the chain steps through which they arise. In the gas phase at subatmospheric pressure at 155°, the principal products are acetone and methanol. Here, the concentration of isobutane is too low to support abstraction (6 in Table VII) in competition with reaction 8. The concentration of isobutane is also too low to support the bimolecular abstraction (9) in competition with the unimolecular cleavage (10). The resulting methyl radicals react with oxygen by an analog of reaction 7 and most of the resulting methylperoxy radicals are converted to methoxy radicals by an analog of reaction 9. As the pressure of isobutane is increased, displacement reactions 6 and 9 begin to replace chain termination and cleavage reactions 10. However, the methylperoxy and methoxy radicals are so much more reactive in chain termination than the corresponding *t*-butylperoxy or *t*-butoxy radicals, either with themselves or with the *t*-butyl derivatives, that a small proportion of surviving methyl radicals and their oxygenated derivatives retards the over-all rate of oxidation. A corresponding effect appeared when we diluted the liquid-phase oxidation with an inert solvent. Cleavage of *t*-butoxy radicals set in and decreased the effective value of $k_p/k_t^{1/2}$ for the liquid phase. Thus, both the gas-phase and the liquid-phase values of $k_p/k_t^{1/2}$ were complicated by methyl radicals from cleavage, and there were too many variables to isolate the effect of phase

Table VII. Products of Oxidation of Isobutane at 100–150°

$$\text{Liquid phase} \longrightarrow \text{mostly } t\text{-BuO}_2\text{H} + \text{some } t\text{-BuOH} + t\text{-Bu}_2\text{O}_2$$

$$t\text{-BuO}_2\cdot + t\text{-BuH} \longrightarrow t\text{-BuO}_2\text{H} + t\text{-Bu}\cdot \tag{6}$$

$$t\text{-Bu}\cdot + \text{O}_2 \longrightarrow t\text{-BuO}_2\cdot \tag{7}$$

$$2t\text{-BuO}_2\cdot \longrightarrow 2t\text{-BuO}\cdot + \text{O}_2 \tag{8}$$

$$t\text{-BuO}\cdot + t\text{-BuH} \longrightarrow t\text{-BuOH} + t\text{-Bu}\cdot \tag{9}$$

Gas Phase
Low pressure ⟶ mostly AcMe + MeOH
High pressure ⟶ increasing proportions of liquid-phase products

$$t\text{-BuO}\cdot \longrightarrow \text{AcMe} + \text{Me}\cdot \tag{10}$$

$$\text{Me}\cdot \xrightarrow{\text{O}_2} \text{MeO}_2\cdot \longrightarrow \text{MeO}\cdot \tag{11}$$

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change. We conclude that the effect of phase change is small in comparison with other complications.

Summary

The rates and products of reactions of free radicals result from competition among several alternative reactions. The commonly large differences in concentration between liquid-phase and gas-phase reactions produce obvious differences in gross rates of reaction. When the most important competing reactions are of different (first and second) order, yields and products are affected as well. Two other aspects of concentration effects can be experimentally important: the cage effect in solution, and the slowing of unimolecular reactions at low pressures. The former can be observed, and the second eliminated, at higher pressures in the gas phase. All of these effects are expected and largely predictable.

The most important contribution of this paper is to emphasize the importance of solvation in reactions of radicals in solution; perhaps there are no really free radicals in solution in the gas-phase sense.[44] Chemists have been slow to recognize this situation because nearly all of our information comes from ratios of rate constants for competing reactions where solvation has similar effects on both. However, in the cleavage and abstraction reactions of alkoxy radicals[42] there is a large and clear effect of solvent and phase change. Even in two reactions as similar as the reaction of a chlorine atom with a primary and a secondary hydrogen atom, an effect has now been detected.[16a] Other examples of solvation were the association of nitrogen dioxide and (in nonradical reactions) the dimerization of cyclopentadiene and the chlorination of isobutylene. It now appears that solvents interact to some extent with all radicals as well as ions and that gas-phase studies are essential to establish the effects of zero solvation in liquid-phase reactions.

Since studies of competing reactions do not tell us whether these reactions are individually accelerated or retarded by solvation, it is important to measure the absolute rate constants for the same reaction at the same temperature in the gas phase and in solution. In further studies of competing reactions, a few more of the most and least polar reactions should be compared in the two phases to see if the distinction between chlorine atoms and alkyl radicals is as sharp as it now seems. The effects of remote substituents[16b,32] seem to be a sensitive tool. Because of the importance of reactions of aryl radicals with aromatic hydrocarbons, further work on the competition of addition and transfer reactions of alkylbenzenes[27,31-35] also seems desirable.

In choosing experimental conditions for practical synthesis through free radicals, the following factors deserve consideration. Liquid-phase reactions require small volumes and favor bimolecular reactions and cage products. Gas-phase reactions usually employ low concentrations which can moderate fast reactions, permit use of high temperatures without high pressures, favor unimolecular reactions, and eliminate cage reactions. High-pressure gas reactions resemble those in the liquid phase. However, the choice of phase depends mostly on consideration of the competing reactions in Table III and how the competition will be affected by phase or concentration changes.

Finally, wall effects are much more important in gas-phase reactions, where diffusion is faster, than in liquid-phase reactions. However, in reactions on walls or in heterogeneous catalysis we are not concerned with free radicals but with bound or complexed radicals which are beyond the scope of this paper.

Acknowledgment. The author appreciates careful readings of this paper and/or numerous useful suggestions by Drs. S. W. Benson, David M. Golden, William A. Pryor, and Cheves Walling.

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Rotation of Styrene and *t*-Butylethylene in Platinum(II) Complexes with 2,4,6-Trimethylpyridine

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Abstract: Several 1,3-dichloro-2-olefin-4-(2,4,6-trimethylpyridine)platinum(II) complexes, **2**, have been prepared and their nmr spectra determined. Although at room temperature there is a single signal for the 2,6-methyl groups, at about −50° the signal splits. This behavior is interpreted to indicate rapid (on the nmr time scale) rotation of the olefinic species about its coordination axis and a "freezing out" at the lower temperature.

In Zeise's anion, **1**, ethylene is known to be oriented at right angles to the square plane in the crystal state.[1] In connection with some other work[2] in this laboratory, we prepared 1,3-dichloro-2-ethylene-4-(2,4,6-trimethylpyridine)platinum(II), **2**, R = H. Although the compound is almost certainly *trans*, the exact spatial arrangement of the ligands with respect to each other is of interest.

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