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# "Reactions in supercritical fluids—a review." Reply to comments

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## Comments on "Reactions in Supercritical Fluids—A Review"

Sir: In a recent review, Subramaniam and McHugh (1986) raise several points concerning the pressure dependence of reaction rates and rate constants in supercritical fluids which we feel need to be clarified. Subramaniam and McHugh's eq 2 is valid for  $k$  expressed as a mole-fraction-based rate constant, as in the review of Eckert (1972), obtained by dividing the conventional rate equation by  $C_t^{n-1}$  and considering the product  $k_c C_t$  as the coefficient,  $k_x$ .

For the conventional rate coefficient, application of transition-state theory yields an equation with an additional term:

$$\left( \frac{\partial \ln k_c}{\partial P} \right)_{T,x} = -\frac{\Delta \bar{V}^\ddagger}{RT} + \left( \frac{1-n}{P} \right) \left[ 1 - \left( \frac{\partial \ln Z}{\partial \ln P} \right)_{T,x} \right] \quad (1)$$

The reported 30% increase of the rate constant with respect to  $P$  for chlorotrifluoroethane dimerization (Simmons and Mason, 1972) was obtained by using eq 1 for  $k_c$ , not Subramaniam and McHugh's eq 2. The second term on the right-hand side of eq 1 often compensates for the activation volume term, therefore limiting the change of  $k_c$  with pressure. This is the reason why such large negative transition-state partial molar volumes are observed near the mixture critical pressure,  $P_c$  (Figure 6 of Subramaniam and McHugh), without correspondingly large changes in  $k_c$ . A comparison of both  $k_c$  and  $k_x$  vs.  $P$  is presented in Figures 1 and 2 for the systems of chlorotrifluoroethane (CTFE) dimerization (Simmons and Mason, 1972), HI decomposition (Kistiakowsky, 1928), and the Menshutkin reaction of triethylamine and ethyl iodide (Kondo, 1968); in the last case  $P_c$  for the mixture is taken as  $P_c$  of the solvent, which was in great excess.

Figure 1 shows that excessively high pressures are not required even for the rate constant  $k_c$  to change significantly and that the changes for all three reactions are gradual and similar functions of reduced pressure. The absence of unusual effects on  $k_c$  or  $k_x$  near the mixture  $P_c$  was also recently observed by Lawson and Klein (1985) for guaiacol hydrolysis to methanol and catechol. Of course,

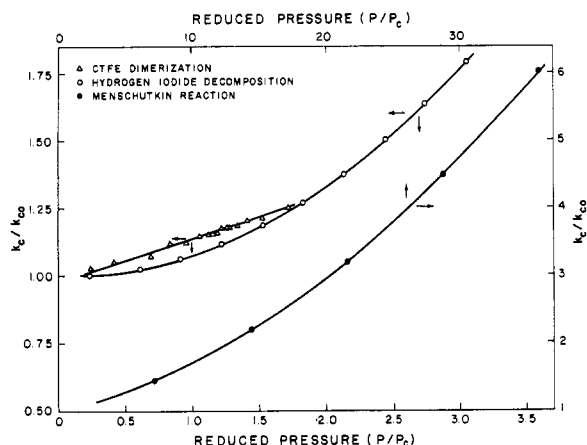


Figure 1.

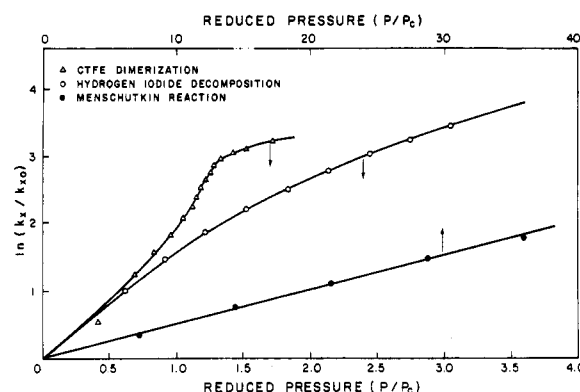


Figure 2.

$k_x$  undergoes more pronounced changes (Figure 2), as follows from its definition. These effects are not limited to the dilute concentration region as implied by Subramaniam and McHugh since the behavior of either  $k_c$  or  $k_x$  in Figures 1 and 2 is similar for all three reactions, two of which involved reactants in high concentration and one of which (the Menshutkin reaction) did not. Also, the effects are not specific to a particular class of bimolecular reactions since the expected transition states of the three reactions are different, in that the reactions are dissimilar:  $A + A \rightarrow B$  (CTFE dimerization);  $A \rightarrow B + C$  (HI decomposition); and  $A + B \rightarrow C + D$  (Menschutkin reaction).

In summary, the reaction rate coefficients  $k_c$  or  $k_x$  can vary significantly with pressure even at moderate reduced pressures, as described by either eq 1 or Subramaniam and McHugh's eq 2 and shown in Figures 1 and 2.

### Nomenclature

- $C_t$  = total concentration
- $k_c$  = concentration-based rate constant
- $k_x$  = rate constant based on mole fraction driving force
- $k_0$  = low-pressure rate constant
- $n$  = molecularity of the reaction
- $P$  = pressure
- $T$  = temperature
- $\Delta \bar{V}^\ddagger$  = difference in partial molar volumes of the activated complex and reactants
- $x$  = mole fraction
- $Z$  = compressibility

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## Response to Comments on "Reactions in Supercritical Fluids—A Review"

Sir: We would like to make the following points in response to the comments of Dooley et al. (1987).

1. We regret the confusion caused by eq 2 in our paper (Subramaniam and McHugh, 1986). We mention this

equation in the paper simply to express the pressure dependence of the kinetic rate constant. Simmons and Mason (1972) make it absolutely clear that  $k_c$  and not  $k_x$  is employed in the analysis of their data.

2. Simmons and Mason (1972) do not directly use Dooley et al.'s eq 1 to calculate the ratio ( $k_c/k_{c0}$ ). Rather, the former employ an equation of state with the following equation to determine  $k_c/k_{c0}$ :

$$k_c/k_{c0} = \phi_R^2 Z / \phi_M$$

3. It is well-known that the variation of  $k_c$  with pressure is much less pronounced than the corresponding variation of  $k_x$  (Mason, 1965). In this context, we would like to point out that for the decomposition of HI ( $T_c = 150^\circ\text{C}$ ,  $P_c = 81\text{ atm}$ ) at  $300^\circ\text{C}$ , a 5-fold increase (from 50 to 250 atm) in absolute pressure causes an approximate 50% increase in  $k_c$  or an approximate 4-fold increase in  $k_x$  (Mason, 1965). Dooley et al.'s Figures 1 and 2 manifest the same results for HI decomposition in terms of reduced rather than absolute pressures. (We think that the ordinate in Figure 2 should be  $k_x/k_{x0}$  and not  $\ln k_x/k_{x0}$ .) Notice that for the Menshutkin reaction, Dooley et al. project an approximate 3-fold increase in  $k_c$  or  $k_x$  for a 3-fold increase in pressure (from  $10P_c$  to  $30P_c$ ) at pressures far removed from the critical point. Thus, the pressure effect on the rate constant is far less pronounced when compared to an Arrhenius temperature effect on the rate constant. We, therefore, do not consider either the above pressure effect on HI decomposition or for similar reasons the reported pressure effects on the chlorotrifluoroethane dimerization and the Menshutkin reaction (Dooley et al., 1987) as being significant. Hence, we differ from Dooley et al. in this regard and still contend that rate enhancements of a larger magnitude than those discussed here (i.e., a magnitude similar to the Arrhenius temperature effect) may be lim-

ited to the dilute concentration region for reasons stated elsewhere (Subramaniam and McHugh, 1986). Obviously, this aspect of rate enhancement in the dilute concentration region needs to be addressed in future research.

### Nomenclature

$k_c$  = molar concentration based second-order rate coefficient  
 $k_x$  = mole fraction based second-order rate coefficient  
 $k_0$  = rate coefficient at low pressures (i.e., as  $Z \rightarrow 1$ )  
 $P_c$  = critical pressure  
 $T_c$  = critical temperature  
 $Z$  = compressibility factor of reaction mixture

Greek Symbol

$\phi_i$  = fugacity coefficient for the species  $i$

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### CORRECTION

**Characterization Parameters for Petroleum Fractions** [Volume 26, Number 4, page 755]. Mohammad R. Riazi and Thomas E. Daubert\*

Page 757. Table V headings for columns 4-9 should read  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ ,  $f$ . In Table VII, the first-row entry under the fifth column, labeled  $b$ , should read  $5.43076 \times 10^{-4}$ .