

Energies and volumes of activation for condensed detonating explosives

Richard D. Bardo, Thomas N. Hall, and Mortimer J. Kamlet

Citation: *The Journal of Chemical Physics* **77**, 5858 (1982); doi: 10.1063/1.443752

View online: <http://dx.doi.org/10.1063/1.443752>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/77/11?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[ACCELERATION AND HEATING OF METAL PARTICLES IN CONDENSED EXPLOSIVE DETONATION](#)

AIP Conf. Proc. **955**, 409 (2007); 10.1063/1.2833077

[Detonation Reaction Zones in Condensed Explosives](#)

AIP Conf. Proc. **845**, 1026 (2006); 10.1063/1.2263497

[Kinetics study of a condensed detonating explosive](#)

J. Chem. Phys. **74**, 5694 (1981); 10.1063/1.440933

[Validity of the Classical Detonation Wave Structure for Condensed Explosives](#)

Phys. Fluids **11**, 1473 (1968); 10.1063/1.1692130

[Calculation of the Detonation Properties of Condensed Explosives](#)

Phys. Fluids **6**, 997 (1963); 10.1063/1.1706858



- ³(a) M. Jacobs and J. Reuss, *Chem. Phys.* **33**, 443 (1978);
 (b) M. Jacobs, J. Reuss, and J. Van de Ree, *ibid.* **51**, 427 (1980).
⁴(a) L. Monchick, *J. Chem. Phys.* **71**, 578 (1979); (b) V. Khare, D. J. Kouri, and D. K. Hoffman, *ibid.* **74**, 2656 (1981); (c) D. E. Fitz, V. Khare, and D. J. Kouri, *Chem. Phys.* **56**, 267 (1981).
⁵S. L. Davis and J. E. Boggs, *J. Chem. Phys.* **69**, 2355 (1978).
⁶S. Green, *J. Chem. Phys.* **73**, 2740 (1980).
⁷S. Green, *J. Chem. Phys.* **64**, 3463 (1976).
⁸A. M. Arthurs and A. Dalgarno, *Proc. R. Soc. London Ser. A* **256**, 540 (1960).
⁹W. A. Lester, Jr., *Meth. Comp. Phys.* **10**, 211 (1971).
¹⁰T. Oka, *Adv. At. Mol. Phys.* **9**, 127 (1973).
¹¹R. M. Lees, *Can. J. Phys.* **53**, 2593 (1975).
¹²M. H. Alexander and P. J. Dagdigian, *J. Chem. Phys.* **66**, 4126 (1977).

COMMENTS

Energies and volumes of activation for condensed detonating explosives

Richard D. Bardo, Thomas N. Hall, and Mortimer J. Kamlet

Naval Surface Weapons Center, White Oak, Silver Spring, Maryland 20910

(Received 2 February 1982; accepted 25 August 1982)

Bdzil *et al.*¹ have obtained, for the first time, bounds on the chemical-kinetic Arrhenius parameters for the shock decomposition of nitromethane at detonation pressures of 22 to 24 GPa. Utilizing measured rates of reaction, these authors estimated ranges of 70–115 kcal/mol for the Arrhenius activation energy and of 10^{16} – 10^{20} s⁻¹ for the pre-exponential factor, and carefully pointed out the pitfalls which can occur when these quantities are used in the interpretation of reaction mechanisms at detonation temperatures and pressures. However, in a comparison of their results with those of other authors, they did not mention that, at high pressures and temperatures, the Arrhenius activation energy may differ significantly from the so-called “true” activation energy by an amount which depends on the volume of activation. In the present note, we wish to clarify and extend their discussion by emphasizing the need for including, in addition to activation energies, the volume of activation in the analysis and identification of reactions at high pressures.

In an analysis of the shock initiation of liquid nitromethane, we have employed an expression which relates the volume of activation V_{act} to the Arrhenius activation energy $E_{\text{act}}^{\text{Arr}}$.² In the following discussion, we shall use the thermodynamic relationship between $E_{\text{act}}^{\text{Arr}}$, V_{act} , and an “internal” or “true” energy of activation ϵ_{act} ,

$$E_{\text{act}}^{\text{Arr}} = \epsilon_{\text{act}} + V_{\text{act}} \left(P - T \frac{dP}{dT} \right), \quad (1)$$

where P and T are the pressure and temperature, respectively, and where

$$E_{\text{act}}^{\text{Arr}} = -R \frac{d \ln k}{d(1/T)}, \quad (2)$$

$$\epsilon_{\text{act}} = -R \left(\frac{\partial \ln k}{\partial (1/T)} \right)_P - PV_{\text{act}}, \quad (3)$$

and

$$V_{\text{act}} = -RT \left(\frac{\partial \ln k}{\partial P} \right)_T. \quad (4)$$

In Eqs. (2)–(4), R is the gas constant and k is the rate coefficient. The quantity ϵ_{act} in Eq. (3) is the change in “internal” energy for the passage of reactants from the initial state to the activated state, which includes changes in potential energy for the associated elementary processes such as bond breaking and formation. The quantity V_{act} in Eq. (4) is the difference in volume between the reactant ground state and activated state. Equation (1) is readily derived from the relationship between the total and partial derivatives which was used in Ref. 2. In Ref. 2, we demonstrated that volumes of activation can be of importance comparable to the energies of activation in the correct interpretation of reaction mechanisms involved in shock and thermal explosion processes. In that study we utilized the data of Hardesty³ for nitromethane at $P \leq 9.2$ GPa and $T \leq 1100$ K. His results indicated that $E_{\text{act}}^{\text{Arr}} \approx 23$ kcal/mol for $7.5 \leq P \leq 9.2$ GPa and $934 \leq T \leq 1100$ K. This low value for $E_{\text{act}}^{\text{Arr}}$ appears to pertain to the shock initiation process. He also obtained two additional very important data points which suggest that, for $P > 9.2$ GPa, $E_{\text{act}}^{\text{Arr}}$ increases sharply from 23 kcal/mol, an indication that a different reaction mechanism takes over. The larger $E_{\text{act}}^{\text{Arr}}$ could fall in the range determined by Bdzil *et al.*¹ for the steady-state detonation process.

While data for $E_{\text{act}}^{\text{Arr}}$ are now available for nitromethane at high pressures in the range $1 \leq P \leq 24$ GPa and at temperatures of $T > 400$ K, little reliable data corresponding to the partial derivatives in Eqs. (3) and (4) are available for $P > 5$ GPa and $T > 400$ K. According to Eq. (1), $E_{\text{act}}^{\text{Arr}}$ itself may differ significantly from ϵ_{act} , depending on the magnitude of $V_{\text{act}}[P - T(dP/dT)]$. Thus, although large changes in $E_{\text{act}}^{\text{Arr}}$ can, indeed, represent changes

in reaction mechanisms, the values of $E_{\text{act}}^{\text{Arr}}$ may appear to be anomalously large or small for activation energies at high pressures and temperatures, while ϵ_{act} and V_{act} maintain physically meaningful values.

At ambient pressure, the factor $f = P - T(dP/dT)$ in Eq. (1) is small, and fV_{act} is generally negligible so that $E_{\text{act}}^{\text{Arr}} \approx \epsilon_{\text{act}}$. For example, the term fV_{act} may be ignored for thermal decomposition studies where the known unimolecular reaction mechanism includes, as the rate-determining step, the homolytic rupture of the C–N bond. Here V_{act} has the low value of $\sim 3 \text{ cm}^3/\text{mol}$ often associated with bond-scission reactions.⁴ In the range of shock pressures considered by Bdzil *et al.*,¹ $22 \leq P \leq 24 \text{ GPa}$, use of their equation of state ($T = 332.5 + 75.3 P + 0.9 P^2$) shows that T and f lie in the ranges $2425 \leq T \leq 2658 \text{ K}$ and $0.9 \leq f \leq 1.6 \text{ GPa}$, respectively. If $V_{\text{act}} \approx 3 \text{ cm}^3/\text{mol}$ at these pressures, $fV_{\text{act}} \approx 1 \text{ kcal/mol}$ is again small when compared with $\epsilon_{\text{act}} = 54 \text{ kcal/mol}$, which we consider to be the most reliable of the many values reported for the above mechanism at ambient pressure.⁵ Although this value for ϵ_{act} appears to lie outside the range of $E_{\text{act}}^{\text{Arr}}$, the existing data do not necessarily allow one to reject this mechanism solely on the basis of Eq. (1). Bdzil *et al.*¹ have pointed out the uncertainties which exist in their bounds on $E_{\text{act}}^{\text{Arr}}$. Moreover, Bdzil and Engelke⁶ have derived an expression for V_{act} , which includes significant nonideal effects for unimolecular reactions at high pressures, and have shown that the effects of fV_{act} on $E_{\text{act}}^{\text{Arr}}$ can be much larger through the reaction zone of a detonation than along the shock Hugoniot.

Unfortunately, the almost total lack of data for ϵ_{act} and V_{act} for reactions at high pressures makes it difficult to choose those values which, through Eq. (1), would be commensurate with the available data for $E_{\text{act}}^{\text{Arr}}$. At the present time, one can only surmise what mechanisms are involved, using data obtained at much lower pressures. On a physical basis, it is likely that the dominant reactions in detonations are accelerated by pressure and, according to Eq. (4), have values of $V_{\text{act}} < 0$. If, e.g., we let $V_{\text{act}} = -10 \text{ cm}^3/\text{mol}$ for nitromethane and assume, say, that $E_{\text{act}}^{\text{Arr}} = 70 \text{ kcal/mol}$ and $P = 24 \text{ GPa}$, we find from Eq. (1) that $\epsilon_{\text{act}} = 74 \text{ kcal/mol}$. The value selected for V_{act} appears reasonable for known reactions which are strongly accelerated by pressures $P < 2 \text{ GPa}$,⁴ and is, e.g., significantly smaller than the difference in volume between the explosive at its starting state and at the von Neumann "spike". With the assumption, then, that large negative values for V_{act} also exist for $P > 2 \text{ GPa}$, it may appear that the calculated activation energy of 74 kcal/mol is too large, when compared with activation energies for many known reactions with

negative volumes of activation. However, caution must be exercised when comparing mechanisms over large ranges of pressure and temperature. This point was also made earlier,² and then more recently⁷ in connection with the results of electronic structure calculations on systems of interacting NO molecules and interacting CH_3NO_2 molecules. These systems behave similarly at high compression in the sense that the low-lying excited electronic states are stabilized to an extent which lowers the bond activation energies, ϵ_{act} . Here, the bond strengths are changed as a result of the intersections among the ground and excited state potential energy surfaces when the molecules are in close proximity. These theoretical studies of the large compression-induced effects on molecular electronic structure complement the work of Drickamer and Frank,⁸ who have demonstrated that pressures in excess of 3 GPa shift electronic states.

It should be noted that Shipitsin⁹ has used an approximation to Eq. (1) in an analysis of thermal explosion data for the explosive HMX (cyclotetramethylene-tetranitramine) at pressures up to 10 GPa . He defines an effective energy of activation E_{eff} , which corresponds to $E_{\text{act}}^{\text{Arr}}$ in Eq. (1) and which includes V_{act} . Using a calculated value of $V_{\text{act}} = -4 \text{ cm}^3/\text{mol}$ at $P = 10 \text{ GPa}$, he finds that E_{eff} is about 10 kcal/mol lower than the activation energy of 38 kcal/mol at ambient pressure.

The principal conclusion of this work is that, once $E_{\text{act}}^{\text{Arr}}$ is known at high pressures and temperatures, the additional steps of determining ϵ_{act} and V_{act} must be taken. When one of these quantities is obtained, the other may be calculated from Eq. (1), using the appropriate P - T equation. Together, ϵ_{act} and V_{act} are useful in interpreting reaction mechanisms in detonations.

¹J. B. Bdzil, R. Engelke, and D. A. Christenson, *J. Chem. Phys.* **74**, 5694 (1981).

²R. D. Bardo, T. N. Hall, and M. J. Kamlet, *Combust. Flame* **35**, 259 (1979).

³D. R. Hardesty, *Combust. Flame* **27**, 229 (1976).

⁴G. Kohnstam, *Prog. React. Kinet.* **5**, 335 (1970).

⁵V. V. Dubikhin, C. M. Nasin, and G. B. Manelis, *Izv. Akad. Nauk SSR, Ser. Khim.* **1339** (1971).

⁶J. B. Bdzil and R. Engelke (to be published).

⁷R. D. Bardo, *Proceedings of the Seventh Symposium (International) on Detonation* (Office of Naval Research, Washington D.C., to be published).

⁸H. G. Drickamer and C. W. Frank, *Electronic Transitions and High-Pressure Chemistry and Physics of Solids* (Chapman and Hall, London, 1973).

⁹L. A. Shipitsin, *Fiz. Goreniya Vzryva* **16**, 85 (1980).