Reply to "'Phantom Activation Volumes' Are Indeed Real Activation Volumes"[†]

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In the preceding article,[1] Weber and van Eldik (W&E) criticized our paper[2] "Phantom Activation Volumes" (PAV). We had reported four examples of increase in rate with rising viscosity of thermal pericyclic reactions: an intermolecular Diels−Alder (DA),[3] an intramolecular DA,[3,4] a 1,3-dipolar cycloaddition (1,3-DC),[3] and a Claisen rearrangement.[4,5] In some cases,[3] our rates rose with viscosity in linear hydrocarbons up to a point (ca. 1.3−2.1 cP) beyond which they declined as solvent chains were extended further.

The rising portion of the viscosity−rate relationship coincides with the increase in viscosity that takes place when volumes of activation (V_a)[6] are determined at high pressure. We pointed out[2] that the negative V_a's for DA, 1,3-DC, and Claisen rearrangements must therefore be the sum of two components: a true V_a[7] and a nonvolume-related "phantom" V_a (PAV) arising from viscosity-induced rate increases. From our own and literature data, we calculated approximate PAV's of 29−61% for 20 intermolecular DA's, 9−21% for 3 intramolecular DA's, 17−26% for 11 1,3-DC's, and 12−28% for 6 Claisen rearrangements. All known cases for which the requisite data are available were included.

W&E[1] repeated one of our four[3−5] viscosity−rate correlations, cyclopentadiene (CPD) dimerization, reporting that they found no acceleration with rising viscosity. Instead, they found a jagged up-and-down relationship (Figure 5), concluding that our data were incorrect and therefore that PAV's do not exist. We will refute W&E on several grounds.

Contrary Data Are Ignored. As stated above, we described four experiments with viscosity-induced accelerations. Chemistry, reaction conditions, reagents, and degree of reversibility were highly varied. Over a 20-year span, one of these (the intramolecular DA)[3,4] was performed by two and one (Claisen)[4,5] by three different chemists, all with concordant results. W&E repeated only one, and mentioned only one other, of these experiments. The other two were not even mentioned.

Previous Literature Is Ignored. W&E completely ignored important literature cited by us that strongly supports our experimental results and general position.

Coster and Pfeil (C&P) reported in 1968 a study[9] in 16 common solvents of the very same reaction, CPD dimerization, for which we and W&E report discordant results. C&P probed for a correlation between rate and any of eight known solvent properties, e.g., dielectric constant, Hildebrand's solvation parameter δ, etc., but without success. However, we found that there is a good correlation in their data between rate and viscosity (Figure 1 in ref 3) in the same range (slope = 0.60−1.28/cP) as ours (1.87/cP). C&P's data thus corroborate ours and not W&E's.

In 1939, a major kinetic study of the same reaction by Wasserman and co-workers[10] provided inter alia these results: rates in a few common solvents vary little and are unrelated to polarity. However, the rate in paraffin oil at 35° exceeds all the others, e.g., twice that in CCl_4, and 2.8 times that in monomeric CPD itself. The rate in dicyclopentadiene exceeds those in CCl_4 and CPD by 2.4× and 3.3×, respectively. These accelerations, which we attribute to viscosity, are close to what we observed (2.5×)[3] in dodecane v−a−v *n*-octane. These data[11] therefore confirm ours and not W&E's. Further confirmation of our thesis is the fact that this reaction proceeds 4.5× faster in paraffin oil than in the gas phase,[10] i.e., across a significant discontinuity in viscosity, a common phenomenon with reactions of similar nature.[4]

Numerous other literature examples of viscosity-induced acceleration have been cited by us (footnotes 8a−f, 13, and 14 in ref 3 and footnotes 6 and 11 in ref 5).

Several cases are of particular interest because the apparent V_a's are so distant from any real physical possibility that the PAV dominates it altogether. In the isoprene−maleic anhydride DA, the apparent V_a at the critical point is -500 cm^3/mol[14] (but read endnote 14). Under similar circumstances, for isoprene + methyl acrylate, the apparent V_a is -750 cm^3/mol.[15] These apparent V_a's cannot be real, for they exceed the total actual volumes of all the reactants severalfold!

Another well-known phenomenon explainable so far only through PAV's is a group of DA's in which the (negative) apparent $|V_a| > |V_r|$, i.e., the TS's appear to be smaller than the cycloadducts.[6] This is physically impossible.[2,8]

Viscosity-*retardation*-derived PAV's have also been observed by Asano's group. In the *Z*−*E* isomerization of indigo the apparent V_a briefly rises to 100 cm^3/mol, physically meaningless because the true V_a is less than 1/10 of this size.[16] This then is a *positive* PAV. In another case, the isomerization of azo compounds and benzylideneaniline, which is normally slowed by high viscosity, shows a strong pressure-induced retardation that arises not from shrinkage, but instead from the increase in viscosity created by the pressure.[17] More examples are cited by le Noble and Asano.[18]

Elsewhere, van Eldik himself-cites a clear example of a positive PAV, termination of free-radical polymerization *retarded* by pressure owing to the pressure-induced rise in viscosity.[19] Homolysis of peroxides, e.g., di-*tert*-butyl peroxide, which are reversible within the solvent cage so that the rate being measured is that for cage escape,[20] also exhibits a positive PAV. "Diffusion control is always characterized by a positive contribution to Va".[18] These positive V_a's are phantom volumes because they arise from pressure-induced changes in viscosity, not volume.

Of course, PAV's are not limited to viscosity effects. Any non-volume-related property of reactants or solvents that influences the rate will give rise to a PAV.[2,21]

Thus, from previous literature alone, it can be seen that PAV's unquestionably exist, and for CPD dimerization, they are commensurate with our own measurements.

Experimental Critique. We hold that anyone wishing to refute another's work should at least repeat it as closely as possible. This W&E have not done. They chose a different temperature, different reagent purification protocol, and different

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[†] Dedicated to Professor Waldemar Adam on his 65th birthday.

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stirring method. Each of these had consequences (v.i.). How convincing is their experimental work? Just because it is more recent does not prove that their data are superior to ours, and in fact, the opposite is true.

"It follows that some of [Swiss and Firestone's] conversions are indeed very low (10−45%) and could possibly lead to large error limits"[1]. We disagree. Our conversions are more than enough to provide accurate rate constants. We chose early time points in order to minimize the retrodiene contribution, and our rate constants are derived from excellent straight lines that are not inferior to W&E's.

W&E's Figure 3 (*n*-decane) shows poor constancy of rate versus reaction progress, with $k_2 \times 10^6$ M^{-1} s^{-1} rising from 1.3 to 1.56, and in Figure 4 (*n*-decane + 1-chlorobutane) $k_2 \times 10^6$ M^{-1} s^{-1} varies enormously, rising from 0.75 all the way to 2.22. Yet in Table 1, these data points are reported as if they were highly precise. For *n*-decane, the rate is given not as 1.43 ± 0.13, which it is, but rather as 1.56 ± 0.03 and 1.53 ± 0.01. For *n*-decane + 1-chlorobutane, the rate is given not as 1.49 ± 0.73, which it is, but instead as 2.25 ± 0.06 and 2.22 ± 0.07. There is no obvious reason they chose to report only the final experimental points in Figures 3 and 4, ignoring the others, especially in view of the incursion of the retrodiene reaction in the late points. Note that in other hands[10] this reaction yielded k_2's that did not change with percent conversion.

W&E report cloudiness in many runs, which they attribute to "the limited solubility of CPD" in some of the solvents. "Jelly-like precipitates" were observed over longer reaction times. In contrast, we found CPD to be quite soluble in all hydrocarbon solvents, and all our runs were crystal-clear at all times. No previous author has ever reported precipitates or cloudiness in this reaction in many varied solvents. Clearly W&E were working with impure reagents or solvents, or both. W&E conclude from Figure 4 that cloudiness raises the rate owing possibly to CPD adsorption onto the precipitate. Yet in Figure 3 the rate is *lower* during the cloudy period.

W&E distilled a new sample of CPD for each run. We regard this as a mistake, as no two samples can be identical owing to the DA reaction that unavoidably accompanies the distillation. Instead, we prepared fresh CPD from time to time, storing it at −78° and using a constant sample for each set of runs in the full series of solvents.

One way of reassuring themselves that they were precisely duplicating our reagents and solvents with no inadvertent errors would have been to measure precisely, as we did, the viscosity of every reaction mixture. However, they did not bother measuring viscosities at all, merely copying our data (from a different temperature, uncorrected!). Surely 10% of 1-chlorobutane ($\eta = 0.422$ cP at 25°) must alter the hydrocarbon viscosities ($\eta = 0.508$ for *n*-octane, >3.41 for *n*-heptadecane at 25°) a great deal, but even in these cases, viscosities were not measured. Clearly the abscissa in Figure 5 is inexact.

The dimerization of CPD, like most DA's, is quite exothermic. Caution must therefore be taken to ensure that heat is created slowly enough that it is readily dissipated to the external bath and that there is no local heat buildup, either in reaction zones not contiguous with the walls of the flask or in smaller random pockets of transiently variable concentration. Any unevenness of temperature will tend to be self-magnifying, thereby creating error in the rate constant. For this reason, we chose the lowest concentration and temperature that produced good data and stirred *from within*. In contrast, W&E chose a higher temperature, thereby increasing the burden of heat dissipation, and stirred by means of a shaker. Stirring a volumetric flask by merely shaking it is inadequate because the entire zone down the middle will never thermally equilibrate with the walls, and smaller thermal inhomogeneities will be slow to dissipate.

In summary, we are quite satisfied to let our study be compared with this one by the scientific community.

References and Notes

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