Solutions to Selected Problems

Problem RK2.7.

1. Scarlet molecules are disappearing over time. Ultramarine molecules are appearing over time. However, the number of scarlet molecules seems to stabilize around half its original number; the number of ultramarine molecules reaches about the same level. It is possible that the scarlet molecules are converted into the ultramarine ones, but reach an equilibrium. At this equilibrium, there happen to be about equal amounts of the two compounds.

2. Because the rate of growth of the tan molecules seems to track the rate of loss of the brown ones, it seems likely that the brown ones are being converted to tan molecules. At some point, the change levels out, so an equilibrium is reached. At this equilibrium, tan molecules outnumber brown ones.

3. Viridian molecules seem to be converting into gold ones but the system reaches equilibrium, at which point there are still more viridian molecules than gold ones.

Problem RK3.3.

a) $e^2 < e^{10}$

b) $e^{1/4} < e^{1/2}$

c) $e^{-3} > e^{-4}$

d) $e^{-1/2} < e^{-1/3}$

Problem RK3.4.

a) Orientation (i) looks most likely to result in connection of the oxygen to carbon with displacement of bromide. In orientation (iii), the oxygen appears ready to collide with the bromine atom. and in orientation (ii), it may collide with a hydrogen atom.

In addition, you will see later that bringing the the oxygen in along the C-Br axis (but away from the bromine) is also more likely to break the C-Br bond, for reasons involving molecular orbital overlap.
b) Orientation (ii) looks like the carbon anion in the acetylide ion is most likely to bond with the carbonyl carbon. In option (i), the carbon is going to collide with the carbonyl oxygen. In option (iii), it may collide with the alpha carbon, next to the carbonyl. Having the nucleophile approach from outside the plane of the carbonyl, as in option (ii), lowers the chance of collision with atoms other than the carbonyl carbon.

Again, there are also molecular orbital reasons that make this approach the preferred one.

**Problem RK3.5.**

1. We would expect the lowest barrier for breaking the Cr-CO bond. The barrier to break the Mo-CO bond would be just slightly lower than to break the W-CO bond.
2. Based on this information alone, we might expect the Cr-CO cleavage to occur most rapidly. Mo-CO cleavage would be slightly faster than W-CO cleavage.

**Problem RK3.6.**

1. On this basis alone, we would expect the lowest barrier for C=C cleavage, followed by C=N and then C=O with the highest barrier.
2. This trend is exactly the opposite of what we just predicted based on bond strengths.
3. There may be a few different reasons for these differences. For example, the electrophilicity of the carbon may be a factor. Based on electronegativity differences, the C=O carbon should be most positive, the C=N carbon less so and the C=C carbon not at all. That electrophilicity may raise the reactant a little in energy.

Alternatively, there may be charge stabilization factors in the first-formed intermediate, which may be reflected in the transition state on the way there. These three differing atoms (O, N, C) are all found in a row of the periodic table, so electronegativity differences should dominate charge stability. The alkoxide ion would be most stable, the amide ion of medium stability and the alkyl anion least stable of all. That trend would lower the barrier to alkoxide formation and raise the barrier to formation of a carbon-based alkyl anion.

**Problem RK4.1.**

The vacancies in the crystal lattices give other atoms places to move into, so they act as a path through which atoms can move. Diffusion through the solid is greatly accelerated.

**Problem RK4.2.**

1. The small, red dots are in the gas phase, so they are distributed throughout the container. The larger, gray dots are the solid, which lies along the bottom of the container.
2. The solid on the left is divided into finer particles, with much more surface area. If the gas reacts on the surface of the solid, reaction will be much faster on the left.
Problem RK4.3.

All three of these solvents have dipole moments. Also, all three molecules have oxygen lone pairs, so they are able to accept hydrogen bonds from hydrogen bond donors.

However, some of the solvents are much more polar than others. Water is capable of donating hydrogen bonds, because of its partially positive hydrogen attached to oxygen. It is the most polar of these solvents.

DMF is also very polar, because it has a polar C=O bond. This particular carbonyl is more like +N=C-O- because of lone pair donation from the nitrogen, so it is quite polar and will interact strongly with other species via dipole-dipole forces (or ion-dipole forces, if the other molecule is a salt).

THF only has a moderate dipole compared to the others. Although it will still interact via dipole-dipole (or ion-dipole) forces, it does so less effectively than water or DMF.

Problem RK4.4.

Water would be a very good solvent for (a) and (d), because both of those molecules would be very good at hydrogen bonding. Although water may be able to dissolve small amounts of the others, their solubility would be limited by the need for water molecules to release hydrogen bonds to each other in order to make room for the non-polar portions of these molecules.

THF would be able to dissolve the other molecules pretty well: (b), (c), (e) and (f). All of those molecules contain polar bonds, like THF, and could interact via dipole-dipole forces. THF would be able to dissolve small amounts of (a) and (d) but may not be polar enough to overcome the stronger intermolecular forces between these molecules.

DMF may be able to dissolve all of these molecules to a moderate extent. Although it is not a protic solvent, its dipole is enough to help overcome hydrogen bonding among (a) and (d).

Contributors

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