Rate and Activation Energy of the Iodination of Acetone

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Abstract:
The rate, rate law and activation energy of the iodination of acetone are determined by observing the disappearance of the characteristic color of iodine in water. By systematically varying the concentration of reactants, the rate law is determined to be first order with respect to acetone and acid, and zero order with respect to iodine: $\text{Rate}_0 = k\,[\text{acetone}]_0\,[\text{HCl}]_0$. Once the rate law expression is found, the activation energy of the reaction is found by measuring the rate of the reaction at multiple temperatures. The calculated activation energy of $92 \pm 11\ ^{kJ}/_{mol}$ is sufficiently large to make the reaction slow enough to observe, but not so large as to make the reaction exceedingly slow.

Introduction:
The activation energy of a chemical reaction is the energy required to initiate collisions energetic enough to allow the transformation of reactants to products and is described by the Arrhenius equation.

$$k = Ae^{\frac{-E_a}{RT}}$$

where:
- k = rate law constant
- A = frequency factor
- E_a = activation energy of the reaction
- R = universal gas constant, $8.314\ ^{J}/_{mol \cdot K}$
- T = temperature in Kelvins

Determination of the rate law constant requires the rate of the reaction to be explored as the initial concentrations of reactants are systematically varied. This allows the orders of the reaction with respect to each reagent to be determined, which is the foundation of the rate law expression.

The iodination of acetone is a convenient reaction to study for a number of reasons: the color of the iodine reactant is characteristic and readily observable, so the change in $[I_2]$ can be easily monitored; the rate of the reaction is fast enough to allow multiple runs during a lab period, but not so fast to be difficult to measure; the reaction is zero-order with respect to iodine so the change in concentration is linear with time. The fact that the reaction is zero order in acetone is especially important because it allows the initial rate of the reaction to be calculated as an *average rate* of the change in iodine concentration over (relatively) long time periods.
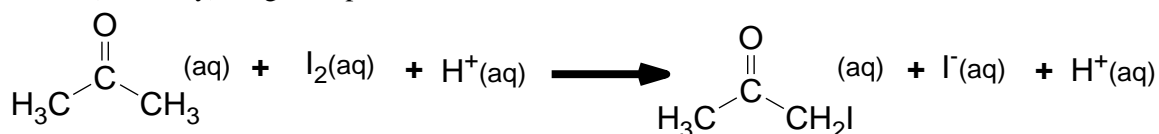
Experimental Procedure:
Determination of the Rate Law Expression:
A number of samples were prepared to explore the dependence of the rate of reaction upon the concentration of reactants, summarized in Table 1. For each sample, the listed volumes of 4.00M acetone solution, 0.990M hydrochloric acid solution, and water were added to one test tube (Tube "A"), and the listed volume of 5.02×10^{-3}M iodine solution was added to a second test tube (Tube "B"). The tubes were placed in a room temperature water bath (20.8°C) and the temperature was allowed to equilibrate for at least 5 minutes.

While the temperature of the samples was stabilizing, the spectrophotometer was calibrated and SpectroPro was set up to collect absorbance vs. time data for 10 minutes, sampling every second. Once the spectrometer was prepared and the samples at temperature, the two tubes were removed from the water bath and data collection was started in SpectroPro as the samples were combined. The mixture was poured back and forth between the two tubes a number of times to mix thoroughly and poured into a small test tube for use in the spectrophotometer. To minimize temperature increases from inside the spectrophotometer, the tube was not placed in the sample compartment until most of the iodine color faded from the reaction solution. The time was recorded when the absorbance reading leveled off at or near zero.

Additional experiments were performed at room temperature, systematically doubling the concentration of reactants while keeping the total sample volume at 8.00mL. For each condition, repeat runs were performed until consistent reaction times were observed.

Determination of the Activation Energy:

Calculation of the activation energy of this reaction requires reaction rate data at additional temperatures. For this experiment, two additional temperature conditions were used. The first was a "cool" bath. A 800mL beaker was filled with water and ice was added to bring the temperature of the bath down to approximately 10°C. The bath was magnetically stirred and temperature was monitored using LoggerPro. Samples were prepared as listed in Table 1 and the tubes were placed in the cool bath to allow the temperature to equilibrate for 5-10 minutes. During equilibration and reaction, the bath temperature was maintained at 9.8±0.1°C. The samples were mixed and immediately returned to the cool bath. This reaction was observed visually, recording the time required for all visible color to fade from the solution. A third temperature condition, the "cold" bath, was also used. For the cold bath, a beaker was filled with ice and enough water was added to facilitate heat transfer. Again, tubes were prepared as described in Table 1 and equilibrated to temperature for 10 minutes before mixing and immediately returned to the cold bath. The temperature of the cold bath was checked periodically and maintained at 0°C by periodic removal of excess water and addition of ice. These samples were also observed visually.

Table 1: Volumes of reagents used and reaction times for each experiment.

Exp't #	Temp. (°C)	Tube A			Tube B	Total Solution Volume, mL	Rxn Time (min)
		mL acetone(aq)	mL HCl(aq)	mL H_2O(l)	mL I_2(aq)		
1	20.8	2.00	2.00	2.00	2.00	8.00	3.72
2	20.8	2.00	2.00	2.00	2.00	8.00	3.70
3	20.8	2.00	2.00	2.00	2.00	8.00	3.82
4	20.8	4.00	2.00		2.00	8.00	1.67
5	20.8	4.00	2.00		2.00	8.00	1.73
6	20.8	4.00	2.00		2.00	8.00	1.80
7	20.8	2.00	4.00		2.00	8.00	1.80
8	20.8	2.00	4.00		2.00	8.00	1.75
9	20.8	2.00	4.00		2.00	8.00	1.82
10	20.8	2.00	2.00		4.00	8.00	7.47
11	20.8	2.00	2.00		4.00	8.00	6.83
12	20.8	2.00	2.00		4.00	8.00	6.98
13*	20.8	2.00	2.00		4.00	8.00	7.12
Cool1	9.8	2.00	2.00	2.00	2.00	8.00	19.25
Cool2	9.8	2.00	2.00	2.00	2.00	8.00	17.47
Cold1	0.0	2.00	2.00	2.00	2.00	8.00	64.07
Cold2	0.0	2.00	2.00	2.00	2.00	8.00	64.77

Notes: All volumes were measured with volumetric pipettes. Measurements were taken at 20.8°C.
*The double-I_2 run was repeated a fourth time because the first three times varied by nearly 10%

Results and Discussion:

Initial concentrations of all reagent were calculated based upon the stock concentrations and the volumes listed in Table 1. Reaction times and concentrations are summarized in Table 2. The rate of the reaction is calculated as the change in concentration of iodine over reaction time, also summarized in Table 2.

Table 2: Initial concentrations and reactions rates for all reactions.

Exp't #	Rxn Time (min)	$[acetone]_0$	$[HCl]_0$	$[I_2]_0$	Reaction Rate (M/min)
1	3.72	1.00	0.248	1.26×10^{-3}	3.37×10^{-4}
2	3.70	1.00	0.248	1.26×10^{-3}	3.39×10^{-4}
3	3.82	1.00	0.248	1.26×10^{-3}	3.29×10^{-4}
4	1.67	2.00	0.248	1.26×10^{-3}	7.15×10^{-4}
5	1.73	2.00	0.248	1.26×10^{-3}	7.25×10^{-4}
6	1.80	2.00	0.248	1.26×10^{-3}	6.97×10^{-4}
7	1.80	1.00	0.495	1.26×10^{-3}	6.97×10^{-4}
8	1.75	1.00	0.495	1.26×10^{-3}	7.17×10^{-4}
9	1.82	1.00	0.495	1.26×10^{-3}	6.90×10^{-4}
10	7.47	1.00	0.248	2.51×10^{-3}	3.36×10^{-4}
11	6.83	1.00	0.248	2.51×10^{-3}	3.67×10^{-4}
12	6.98	1.00	0.248	2.51×10^{-3}	3.60×10^{-4}
13	7.12	1.00	0.248	2.51×10^{-3}	3.53×10^{-4}
Cool1	19.25	1.00	0.248	1.26×10^{-3}	6.52×10^{-5}
Cool2	17.47	1.00	0.248	1.26×10^{-3}	7.18×10^{-5}
Cold1	64.07	1.00	0.248	1.26×10^{-3}	1.959×10^{-5}
Cold2	64.77	1.00	0.248	1.26×10^{-3}	1.938×10^{-5}

Sample Calculations for Table 2 values:
Initial concentration of acetone, run 1:

$$[\text{acetone}]_{\text{initial}} = \frac{[\text{acetone}]_{\text{stock}} (\text{volume of acetone})_{\text{stock}}}{(\text{volume of solution})_{\text{total}}} = \frac{(4.00\text{M})(2.00\text{mL})}{8.00\text{mL}} = 1.00\text{M}$$

Initial concentration of hydrochloric acid, run 1:

$$[\text{HCl}]_{\text{initial}} = \frac{[\text{HCl}]_{\text{stock}} (\text{volume of HCl})_{\text{stock}}}{(\text{volume of solution})_{\text{total}}} = \frac{(0.990\text{M})(2.00\text{mL})}{8.00\text{mL}} = 0.248\text{M}$$

Initial concentration of iodine, run 1:

$$[\text{I}_2]_{\text{initial}} = \frac{[\text{I}_2]_{\text{stock}} (\text{volume of I}_2)_{\text{stock}}}{(\text{volume of solution})_{\text{total}}} = \frac{(5.02\text{x}10^3\,\text{M})(2.00\text{mL})}{8.00\text{mL}} = 1.26\text{x}10^3\,\text{M}$$

Rate of reaction, run 1:

$$\text{Rate of reaction} = -\frac{\Delta[\text{I}_2]}{\Delta t} = -\frac{[\text{I}_2]_{\text{final}} - [\text{I}_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} = -\frac{0\text{M} - 1.26\text{x}10^{-3}\,\text{M}}{3.72\text{min}} = 3.37\text{x}10^{-4}\,\tfrac{\text{M}}{\text{min}}$$

For analysis of the orders of reaction in the rate law expression, it is convenient to use average reaction rates for each set of conditions. The conditions are summarized in Table 3 as averages.

Table 3: Average reaction rates for each set of conditions.

	$[\text{acetone}]_0$	$[\text{HCl}]_0$	$[\text{I}_2]_0$	Reaction Rate ($\tfrac{\text{M}}{\text{min}}$)	Error on the average rate
Standard Run	1.00	0.248	$1.26\text{x}10^{-3}$	$3.35\text{x}10^{-4}$	$\pm0.05\text{x}10^{-4}$ (1.5%)
Double acetone	2.00	0.248	$1.26\text{x}10^{-3}$	$7.3\text{x}10^{-4}$	$\pm0.3\text{x}10^{-4}$ (4.1%)
Double acid	1.00	0.495	$1.26\text{x}10^{-3}$	$7.01\text{x}10^{-4}$	$\pm0.14\text{x}10^{-4}$ (2.0%)
Double iodine	1.00	0.248	$2.51\text{x}10^{-3}$	$3.54\text{x}10^{-4}$	$\pm0.16\text{x}10^{-4}$ (4.5%)
Cool Runs	1.00	0.248	$1.26\text{x}10^{-3}$	$6.9\text{x}10^{-5}$	$\pm0.3\text{x}10^{-5}$ (4.3%)
Cold Runs	1.00	0.248	$1.26\text{x}10^{-3}$	$1.948\text{x}10^{-5}$	$\pm0.011\text{x}10^{-5}$ (0.6%)

The consistently sub-5% errors on these average reaction rates indicate that the data should be quite reliable for determination of the rate law expression and the activation energy of the reaction.

Comparing the standard run to the double acetone run, the rate of the reaction approximately doubled when the initial concentration of acetone doubled; therefore, the reaction is first order with respect to acetone.

Comparing the standard run to the double acid run, the rate of the reaction approximately doubled when the initial concentration of acid doubled; therefore, the reaction is first order with respect to acid.

Comparing the standard run to the double iodine run, the rate of the reaction is unchanged when the initial concentration of iodine doubled; therefore, the reaction is zero order with respect to iodine.

Therefore, the rate law expression for this reaction is:

$$\text{Rate}_0 = k\,[\text{acetone}]_0^1\,[\text{HCl}]_0^1\,[\text{I}_2]_0^0 = k\,[\text{acetone}]_0\,[\text{HCl}]_0$$

The exact mathematical value of the rate law orders can also be found to indicate the error in these measurements.
Comparing the standard run to the double acetone run:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{3.35\text{x}10^{-4}\,\tfrac{\text{M}}{\text{min}}}{7.3\text{x}10^{-4}\,\tfrac{\text{M}}{\text{min}}} = \frac{k(1.00\text{M})^x(0.248\text{M})^y(1.26\text{x}10^{-3}\,\text{M})^z}{k(2.00\text{M})^x(0.248\text{M})^y(1.26\text{x}10^{-3}\,\text{M})^z} = \frac{k[\text{acetone}]_1^x[\text{HCl}]_1^y[\text{I}_2]_1^z}{k[\text{acetone}]_2^x[\text{HCl}]_2^y[\text{I}_2]_2^z}$$

$$\ln\frac{3.35\text{x}10^{-4}\,\tfrac{\text{M}}{\text{min}}}{7.3\text{x}10^{-4}\,\tfrac{\text{M}}{\text{min}}} = \ln\frac{(1.00\text{M})^x}{(2.00\text{M})^x} = \ln\left(\frac{1}{2}\right)^x = x\ln\left(\frac{1}{2}\right)$$

$$x = 1.11$$

Comparing the standard run to the double acid run:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{3.35\text{x}10^{-4}\,\tfrac{\text{M}}{\text{min}}}{7.01\text{x}10^{-4}\,\tfrac{\text{M}}{\text{min}}} = \frac{k(1.00\text{M})^x(0.248\text{M})^y(1.26\text{x}10^{-3}\,\text{M})^z}{k(1.00\text{M})^x(0.495\text{M})^y(1.26\text{x}10^{-3}\,\text{M})^z} = \frac{k[\text{acetone}]_1^x[\text{HCl}]_1^y[\text{I}_2]_1^z}{k[\text{acetone}]_2^x[\text{HCl}]_2^y[\text{I}_2]_2^z}$$

$$\ln\frac{3.35\text{x}10^{-4}\,\tfrac{\text{M}}{\text{min}}}{7.01\text{x}10^{-4}\,\tfrac{\text{M}}{\text{min}}} = \ln\frac{(0.248\text{M})^y}{(0.495\text{M})^y} = \ln\left(\frac{1}{2}\right)^y = y\ln\left(\frac{1}{2}\right)$$

$$y = 1.07$$

Comparing the standard run to the double iodine run:

$$\frac{Rate_1}{Rate_2} = \frac{3.35 \times 10^{-4} \frac{M}{min}}{3.54 \times 10^{-4} \frac{M}{min}} = \frac{k(1.00M)^x (0.248M)^y (1.26 \times 10^{-3} M)^z}{k(1.00M)^x (0.248M)^y (2.51 \times 10^{-3} M)^z} = \frac{k[acetone]_1^x [HCl]_1^y [I_2]_1^z}{k[acetone]_2^x [HCl]_2^y [I_2]_2^z}$$

$$\ln \frac{3.35 \times 10^{-4} \frac{M}{min}}{3.54 \times 10^{-4} \frac{M}{min}} = \ln \frac{\left(1.26 \times 10^3 M\right)^z}{\left(2.51 \times 10^3 M\right)^z} = \ln\left(\frac{1}{2}\right)^z = z \ln\left(\frac{1}{2}\right)$$

$$z = 0.079$$

These calculated orders are all very close to the qualitatively determined orders, so these experimental results do not have significant error, as reflected in the average reaction rates in Table 3.

The value of the rate law constant is found by plugging the concentration and rate data back into the rate law expression and solving for k.

Table 4: Rate law constants

Exp't #	$[acetone]_0$	$[HCl]_0$	$[I_2]_0$	Reaction Rate ($\frac{M}{min}$)	k ($M^{-1}min^{-1}$)
1	1.00	0.248	1.26×10^{-3}	3.37×10^{-4}	1.36×10^{-3}
2	1.00	0.248	1.26×10^{-3}	3.39×10^{-4}	1.37×10^{-3}
3	1.00	0.248	1.26×10^{-3}	3.29×10^{-4}	1.33×10^{-3}
4	2.00	0.248	1.26×10^{-3}	7.15×10^{-4}	1.52×10^{-3}
5	2.00	0.248	1.26×10^{-3}	7.25×10^{-4}	1.47×10^{-3}
6	2.00	0.248	1.26×10^{-3}	6.97×10^{-4}	1.41×10^{-3}
7	1.00	0.495	1.26×10^{-3}	6.97×10^{-4}	1.41×10^{-3}
8	1.00	0.495	1.26×10^{-3}	7.17×10^{-4}	1.45×10^{-3}
9	1.00	0.495	1.26×10^{-3}	6.90×10^{-4}	1.39×10^{-3}
10	1.00	0.248	2.51×10^{-3}	3.36×10^{-4}	1.36×10^{-3}
11	1.00	0.248	2.51×10^{-3}	3.67×10^{-4}	1.48×10^{-3}
12	1.00	0.248	2.51×10^{-3}	3.60×10^{-4}	1.45×10^{-3}
13	1.00	0.248	2.51×10^{-3}	3.53×10^{-4}	1.42×10^{-3}
Cool1	1.00	0.248	1.26×10^{-3}	6.52×10^{-5}	2.63×10^{-4}
Cool2	1.00	0.248	1.26×10^{-3}	7.18×10^{-5}	2.90×10^{-4}
Cold1	1.00	0.248	1.26×10^{-3}	1.959×10^{-5}	7.91×10^{-5}
Cold2	1.00	0.248	1.26×10^{-3}	1.938×10^{-5}	7.83×10^{-5}

For Exp't 1:

$$Rate_0 = k [acetone]_0 [HCl]_0$$
$$3.37 \times 10^{-4} \, ^M/_{min} = k (1.00M) (0.248M)$$
$$k = 1.36 \times 10^{-3} \, M^{-1}min^{-1}$$

The value of k should be constant for a reaction at each temperature, so the k values are averaged for each temperature, results are shown in Table 5.

Table 5: Average rate law constants at three temperatures

Temperature (K)	Average k, $M^{-1}min^{-1}$	Error on average k
294.0	1.42×10^{-3}	$\pm 0.10 \times 10^{-3}$ (7.0%)
283.0	2.77×10^{-4}	$\pm 0.14 \times 10^{-4}$ (5.1%)
273.2	7.87×10^{-5}	$\pm 0.04 \times 10^{-5}$ (0.51%)

The activation energy of this process can be determined by using the Arrhenius equation. Given the data in Table 5, the comparative form of the Arrhenius equation can be used three times to determine the activation energy of this process.

$$\ln\left(\frac{k_1}{k_2}\right) = \left(\frac{E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Comparing the room temperature and cool data:

$$\ln\left(\frac{1.42 \times 10^3 \frac{1}{M \cdot min}}{2.77 \times 10^4 \frac{1}{M \cdot min}}\right) = \left(\frac{E_a}{8.314 \frac{J}{mol \cdot K}}\right)\left(\frac{1}{283.0K} - \frac{1}{294.0K}\right)$$

$$E_a = 1.03 \times 10^5 \, ^J/_{mol} = 103 \, ^{kJ}/_{mol}$$

Comparing the room temperature and cold data:

$$\ln\left(\frac{1.42 \times 10^3 \, \frac{1}{M \cdot min}}{7.87 \times 10^5 \, \frac{1}{M \cdot min}}\right) = \left(\frac{E_a}{8.314 \frac{J}{mol \cdot K}}\right)\left(\frac{1}{273.0K} - \frac{1}{294.0K}\right)$$
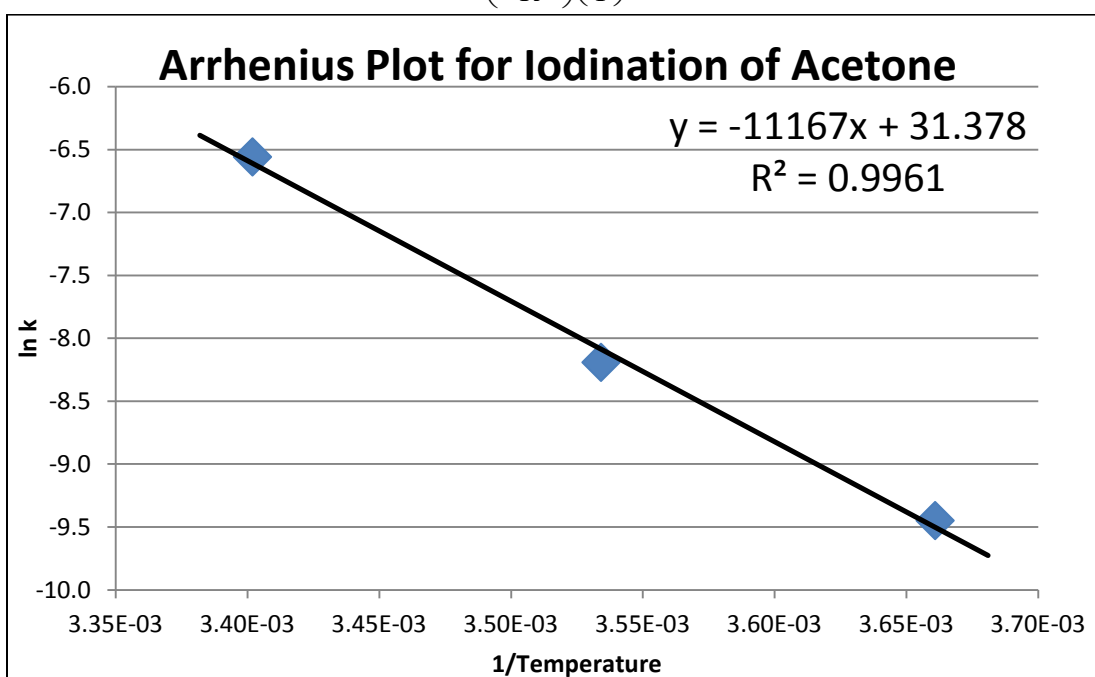
$$E_a = 9.19 \times 10^4 \, ^J/_{mol} = 91.9 \, ^{kJ}/_{mol}$$

Comparing the cool and cold data:

$$\ln\left(\frac{2.77 \times 10^4 \, \frac{1}{M \cdot min}}{7.87 \times 10^5 \, \frac{1}{M \cdot min}}\right) = \left(\frac{E_a}{8.314 \frac{J}{mol \cdot K}}\right)\left(\frac{1}{273.0K} - \frac{1}{283.0K}\right)$$

$$E_a = 8.08 \times 10^4 \, ^J/_{mol} = 80.8 \, ^{kJ}/_{mol}$$

The average activation energy is $92 \pm 11 \, ^{kJ}/_{mol}$ based upon pairwise data. This 12% error seems high, but this is largely a result of using a relatively small temperature range for the experiments. As can be seen in the data, the calculated activation energy for the largest temperature change (room temperature to cold) is most consistent with the average, while the smaller room-cool and cool-cold values vary significantly. The activation energy can also be calculated graphically using the linear form of the Arrhenius equation.

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

Arrhenius Plot for Iodination of Acetone

y = -11167x + 31.378
R² = 0.9961

$$\text{slope} = -11167K = \frac{-E_a}{8.314 \frac{J}{mol \cdot K}} = \frac{-E_a}{R}$$

$$E_a = 9.28 \times 10^4 \, ^J/_{mol} = 92.8 \, ^{kJ}/_{mol}$$

The value of the activation energy determined from the linear form of the Arrhenius equation is in very close agreement with that found from the pair-wise treatment of the data, with less than 1% difference between the two methods. A more reliable analysis of the activation energy could be done with a larger temperature range and/or more temperatures.

Conclusions:
Determination of the rate law and activation energy of a chemical reaction requires a number of steps. By varying the concentrations of reactants in the iodination of acetone it was determined that the reaction is first order with respect to both acetone and hydrochloric acid concentration and zero order with respect to iodine concentration. Measuring the reaction rate at multiple temperatures allows calculation of the activation energy of the process, in this case the activation energy of the reaction is found to be $92 \, ^{kJ}/_{mol}$. The error in all parts of this experiment is relatively small. This reaction is fast enough to be performed in a reasonable amount of time, but not so fast that it is difficult to measure. This means that the calculated activation energy, $92 \, ^{kJ}/_{mol}$, is a moderate barrier to reaction.