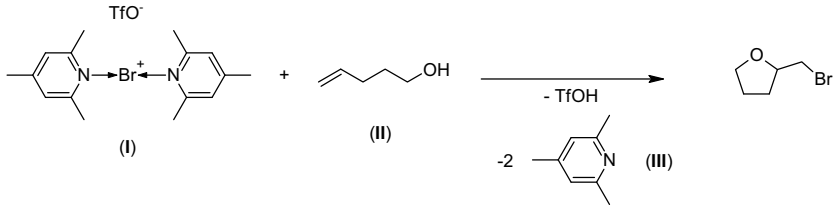
1. Mechanisms of Organic Transformations

Carefully designed kinetic experiments can contribute a great deal of information to understanding mechanisms of organic transformations. The reaction of stabilized bromonium trifuoromethanesulfonate ($F_3CSO_3^-$, conjugated base of a very strong acid, commonly abbreviated as TfO^-) **I** with pent-4-ene-1-ol (**II**) provides the cyclic product shown below.



1. Under flooding conditions (huge excess) in II and collidine (III), the reaction is first order with respect to I (flooding of both of these reagents is required to achieve 1st order kinetics).
2. The rate of product formation is inhibited by the addition of excess collidine (III).
3. A plot of k_{obs} (observed rate constant) vs. [II] shows "saturation kinetics", and a related plot of $1/k_{obs}$ vs. [III]/[II] was linear.
4. The rate of product formation is not affected by the addition of excess TfO^-.

Based on this data

a) Propose a mechanism for this transformation.

b) Derive a rate expression for the formation of product (d[product]/dt) that is consistent with this mechanism (several plausible mechanisms can be derived based on the aforementioned observations).

c) Propose a modification of the substrate I that you would expect to accelerate this reaction based on the mechanism you proposed.

2. Spectroscopic Signatures of Halogens

Dihalogen molecules are often employed as spectroscopic model systems due to their intense optical spectra. The electronic states involved in the valence band spectra are sketched in Figure 1. Two overlapping transitions produce the observed gas-phase absorption band shown in Figure 2. Transition $^1\Pi_u \leftarrow {}^1\Sigma_g$ is spin forbidden, while $^3\Pi_u \leftarrow {}^1\Sigma_g$ is nominally spin-forbidden; in each case, an electron is promoted from the antibonding π^* orbital to the antibonding σ^* orbital.

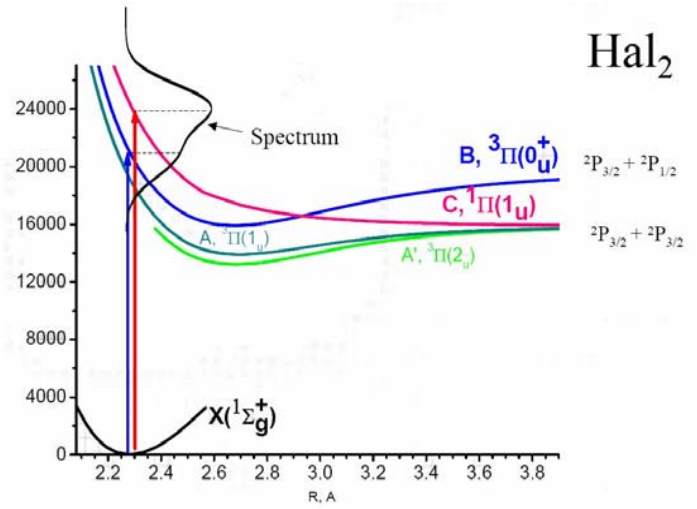


Figure 1.

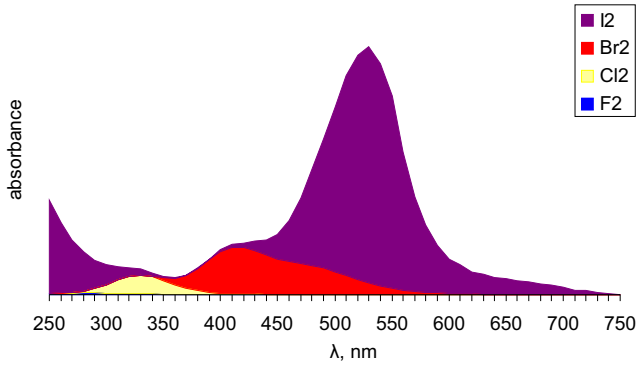


Figure 2.

Unfortunately, spectroscopy of molecules in general gives information on the energy difference between the initial and final states rather than the energy levels involved in the transition. However, the energy of both occupied and unoccupied molecular orbitals is of particular interest to chemists.

a) Give a relative energy diagram for the MO's of halogens which possess only *n*s and *n*p electrons. Mark by arrow allowed transitions.

b) Using MO theory, explain, why the position of the absorption maximum shifts to the red.

c) Predict the positions of the absorption maximums (±50 nm) of BrCl, ICl, IBr in visible spectra.

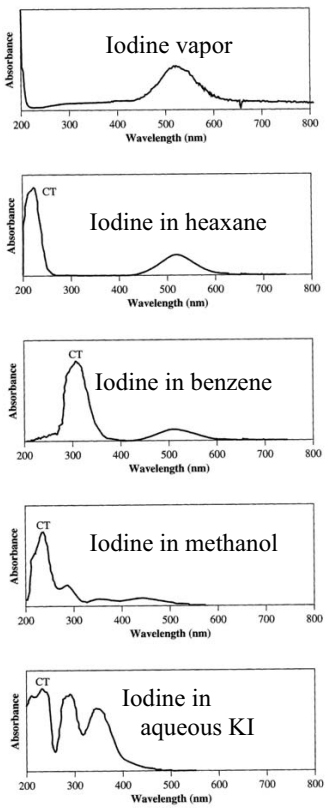


Figure 3. (λ vs. abs.)

In various solvents halogens change colour. The Figure 3. represents the absorption spectra of different solutions of I_2, and also gas-phase absorption spectra of I_2.

d) Give a relative energy diagram for the MO's of I_2-solvent. Mark by arrows transitions, which produce visible absorption and correspond to CT (charge transfer).

e) Using MO theory, explain, why the position of the absorption maximum shifts to the blue in the given series.

UV-vis spectroscopy has been used in study of halogen's molecules confined in clathrate hydrate cages. Scientist found a unique spectroscopic signature that distinguishes halogens in clathrate hydrates from halogens in ice. For bromine there is almost no shift of the halogen absorption spectrum relative to the gas phase one (300 cm^{-1}), while there is a 1400 cm^{-1} spectral shift of the bromine in ice. That is because:

1. all of the oxygen lone pair electrons in the clathrate hydrate cages are included in hydrogen bonds and are thus unavailable for donation to the bromine molecules.

2. of the greater overlap of bromine's and oxygen's orbitals in clathrate hydrate cages due to the structure compression.

f) Mark the correct answer.

3. Purity of Hydrazine

Purity of the hydrazine N_2H_4 (NB! Be careful, poisonous!) could be determined by the iodine titration. Oily liquid with a mass of 1.4286 g was dissolved in 1.000 l of water. 42.41 ml of standard iodine solution was required to titrate 50.00 ml of the obtained solution. Iodine solution was standardized with the As_2O_3 solution, which was prepared from 0.4123 g As_2O_3 by dissolving it in a small quantity of NaOH solution with pH = 8. 40.28 ml of iodine solution was required for the titration of this solution.

a) Calculate the percentage of hydrazine in the sample.

b) Draw the Lewis structure of As_2O_3.

c) Draw its structure using VSERP method. Determine the geometry of atom arrangement around the arsenic and oxygen atoms.

4. Self destructing paper

Old books are very important cultural heritage of nation's history. But USA is losing this treasure, soon 40% of the books will be too fragile to handle. Problem of this fact hides in the paper of these books. In XIX paper manufacturers found that it is useful to add $Al_2(SO_4)_3$ into paper but this compound causes self destruction of the paper.

a) What ion does form from Al^{3+}? Write the equation of this process.

b) What properties (acidic or basic) this new formed ion has? Show them by reaction equation.

c) Same ion forms in aqueous $Al(NO_3)_3$ solution. Ionization degree of this hydrated ion is 52.9% and pH of this solution is 5.00. Calculate pK_a of this ion.

d) Calculate pH of 0.200 M $Al(NO_3)_3$ solution.

e) One page of a book maid from paper manufactured using $Al_2(SO_4)_3$ contains 0.86 mg of it. Book of 500 pages was dipped into 5.0 l volume of water and all alum dissolved. 1,0 ml of this solution was taken and pipetted into 1.0 l flask filled with distilled water. Calculate pH of this solution. (When solving this problem you may get a third power equation and you may use approximate methods of solving. One of them: http://en.wikipedia.org/wiki/Newton's_method).

5. Automobile engine

Energy efficiency is the issue of the XXI century. Let's examine the principle of operation of gasoline engine. Work cycle of four-strouke engine (Otto's cycle) consists of four steps (Figure 4.):

Step one. Cycle begins with the intake stroke *5* → *1*, which is assumed to take place at constant pressure.

Step two. At point *1*, the intake valve is closed, and the piston compresses the fuel-air mixture along the adiabatic path *1* → *2*.

Step three. Ignition of the fuel-air mixture takes place at *2*. The rapid increase on pressure takes place at essentially a constant volume. The power stroke is modeled as the adiabatic expansion *3* → *4*.

Step four. At point *4*, the exhaust valve opens and the gas is expelled. This step is modeled as the constant volume pressure decrease *4* → *1*. Otto cycle ends when the upward piston expels the remainder of the gas along the line *1* → *5*, after which the cycle begins again.

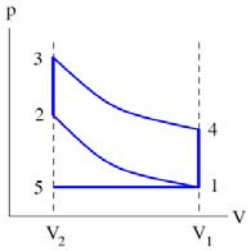


Figure 4.

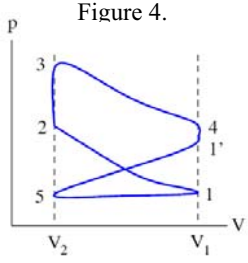


Figure 5.

a) Draw the diagram of engine work (1→2→3→4→1) in coordinates V–S и T–V.

It is quite difficult to design a real engine (Figure 5.). If we suppose that all gases act as ideal ones, that there is no heat exchange with the environment, and that heat capacity does not depend on temperature; we shall obtain a very unrealistic result. In order to calculate the operating efficiency of car engine, we should know the value of the constant volume heat of combustion – ΔU. We may assumed that $\Delta H_r^T \approx \Delta H_r^\circ$, and $\Delta U_r^T = \Delta H_r^T - \Delta n_{gas} RT$.

b) Calculate the value of ΔU_r^{700}.

	Isooctane (l)	O_2 (g)	N_2 (g)	CO_2 (g)	H_2O (l)
S°, $J \cdot K^{-1} \cdot mol^{-1}$	328.11	205.15	191.61	213.79	69.94
ΔH_f°, $J \cdot mol^{-1}$	−259.16	0	0	−393.51	−285.83
ΔH_{vap}°, $J \cdot mol^{-1}$	35.15	–	–	–	44.00

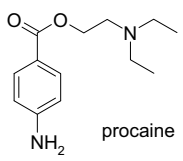
Nowadays, stochiometric composition of fuel-air mixture is being used in gasoline/petrol engines. Let's assume that air contains 21% (vol.) O_2 and 79% N_2, considering that fuel is pure isooctane. At point *1* temperature is 100°C, cylinder volume equals 0.35 litre.

c) Calculate the quantity of heat Q_r obtained in the reaction of fuel combustion in one cylinder, in one cycle.

d) Calculate the operating efficiency of petrol engine, assuming that leaving gases (4 → 1 → 5) take away approximately 490 J during one cycle.

e) Efficiency of internal-combustion engines is quite small. For a comparison calculate the efficiency of isooctane combustion in a fuel cell at 25°C.

6. Chemistry of Anesthesia



procaine

1. The first local anesthetic was isolated from leaves of the coca shrub. Named cocaine, its first documented use in medicine occurred in 1884, when the opthamologist Carl Koller applied it to the surface of the eye. In 1892, the German chemist Einhorn took up the challenge of replacing this toxic and addictive substance with a suitable synthetic amino ester, even though questions regarding cocaine's structure were not completely answered until 1901. Einhorn's efforts culminated in 1906 with the preparation of procaine (**4**). Conversion of p-nitrobenzoic acid (**1**) to the chloroethyl ester (**2**) via the SO_2Cl_2 then $HOCH_2CH_2Cl$ was followed by S_N2 amination of the side chain with diethylamine to furnish intermediate (**3**). Classical reduction of the ring nitro with an active metal completed the preparation of procaine (**4**). **a)** Write down synthesis scheme of procaine.

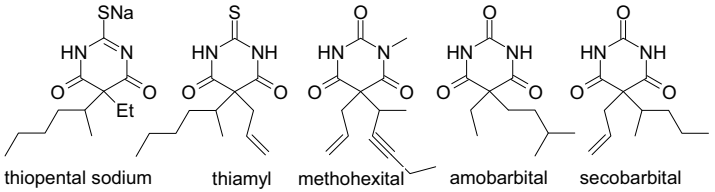
2. The first commercial sedative–hypnotic barbiturate, barbital or 5,5-diethylbarbituric acid, appeared in 1904, and the straightforward preparation of other barbiturates from diethyl malonate, was repeated countless times. Thiopental sodium (**8**) was the first of the intravenous induction (ultrashort-acting) anesthetics; thiamylal (**9**) and methohexital (**13**) sodium would also find use in this way.

2.1. Via the S_N2 C-alkylation of the enolate anion of diethyl malonate with the secondary alkyl halide, 2-bromopentane, monoalkylated malonate ester (**5**) was formed. A second

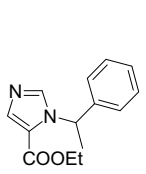
alkylation with ethyl bromide or allyl bromide yielded the disubstituted malonate ester **6** or **7**. Ring formation then occurred as the two nucleophilic nitrogen atoms of thiourea bonded to two electrophilic ester carbonyls. The emergence of a stable charge-delocalized anion (seen in structure **8** but not in **9**) helps to bring this reaction to completion. **b)** Write down synthesis schemes of thiopental sodium and thiamylal.

2.2. Presence of the carbon–carbon triple bond in one side chain of methohexitol required the preliminary synthesis of 2-bromo-3-hexyne (**11**). A Grignard reaction between acetaldehyde and 1-butynylmagnesium bromide led to 3-hexyn-2-ol (**10**). Careful treatment of **10** with phosphorous tribromide and pyridine then gave the alkylating agent (**11**). Stepwise alkylation of the enolate anion of ethyl cyanoacetate with 3-hexyn-2-ol then allyl bromide gave disubstituted malonate ester (**12**). Methohexital (**13**) formed by treatment of **12** by methylurea. **c)** Write down synthesis scheme of methohexital.

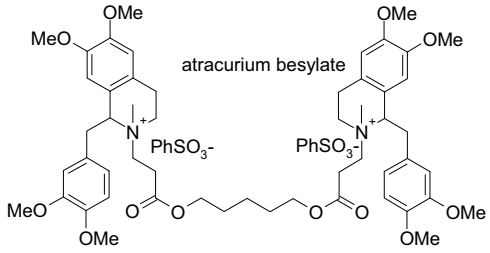
2.3. **d)** Propose synthesis schemes of classic sedative–hypnotic barbiturates amobarbital and secobarbital.



3. Rather than a barbiturate many anesthesiologists today are turning to propofol as an induction anesthetic. Etomidate is similar agent that find more limited use. The pathway to etomidate (**17**), involves four separate reaction steps. N-alkylation of α-methylbenzylamine with ethyl chloroacetate in the presence of triethylamine leads to the N-substituted glycinate ester (**14**). The N-formylation of **14** in refluxing formic acid followed by a mixed Claisen condensation leads to the multifunctional compound **15**. Ring closure occurs as **15** reacts with thiocyanic acid (HNCS) to form the methyl ester of 1-(α-methylbenzyl)-2-mercaptoimidazole-5-carboxylic acid, **16**. Oxidative removal of the sulfur is followed by saponification, acid chloride formation, and a final reaction with ethanol to yield the ethyl ester known as etomidate (**17**). **e)** Write down synthesis scheme of etomidate.



etomidate



4. As produced commercially atracurium besylate (**18**) is a mixture of stereoisomers. **f)** How many stereoisomers of **18** may be in mixture?